

Heavy Metal Archaeology

An Examination of Lead's Significance for the
Interpretation of Archaeological Bone

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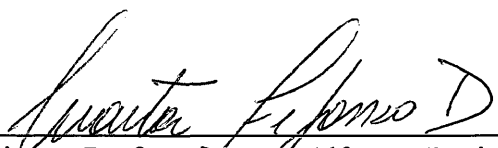
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ABSTRACT PAGE

Recent methodological advances in the analysis of archaeological bone have permitted researchers to characterize the interface of biology and culture in ways previously thought impossible. Physicochemical assays of archaeologically-recovered bone can contribute significantly to anthropological dialogue, revealing information otherwise unobtainable by traditional visual or metric analyses. Trends in the application of scientific methodologies to archaeology have led many researchers to consider the implications that trace elements, sequestered in the skeletal tissues, have for archaeological interpretations. Trace elements provide a nuanced and very insightful avenue for investigation, as their role as minute, metabolized artifacts has variously served to corroborate or contradict traditional understandings of past places and peoples. One element in particular, lead, has been of keen interest to recent generations of archaeologists. Toxic to humans and easily metabolized with minimal exposure, lead's occurrence in human tissue is often indicative of some form of cultural acquisition. Furthermore, the heavy metal's importance to technological processes in Western culture makes it an ideal element of study. However, while it would be difficult to understate lead's importance to biological archaeology, the management of its anthropological implications has at times been misguided. Too often have results obtained from lead analysis given way to short-sighted conclusions about cultural practice. The science of trace element detection cannot be considered diagnostic of any cultural trait, but rather must be viewed as a supplement to alternative lines of evidence. It is therefore the purpose of this paper not only to address lead's interaction with skeletal tissues and burial environments, but to critically examine ways in which lead has been used in drafting archaeological conclusions. Furthermore, a case study will be introduced for which a potential lead-based analysis could be conducted with the ultimate purpose of instructing how such testing might be more appropriately used in archaeological interpretation. It is hoped that by such an assessment, lead's value to archaeologists will be made clear, but tempered to accommodate a more realistic vision of its overall contributions to the field.

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INTRODUCTION

Archaeology is commendable as an academic discipline for, among other things, its emphasis on the merits of holistic research. In borrowing principles and methodologies from a variety of other fields, archaeological inquiry continues to deepen our understanding of, and appreciation for, past peoples and the cultures they embodied. Clearly, then, archaeology is a humanistic enterprise, and ought to be celebrated for the elegance of its aesthetics and ingenuity of its investigators.

The use of scientific experiments in archaeological inference may seem, at first, misplaced positivism in the art of interpreting past human experiences. But the methodical scrutiny of science can be highly complimentary to archaeology, and anthropological contributions from biology, physics, and chemistry are manifold. Provided that the data obtained in a laboratory supplement, and not supersede other lines of evidence, chemical or physical assays can reveal informational subtleties not immediately apparent on the edge of a trowel. Any tool an investigator can use to modify their reasoning ought to be taken up, and given the complexity of certain archaeological materials, scientific study sometimes offers the best means.

This is particularly true when an archaeologist grapples with the physical remains of the people he or she is studying. Human bone is a remarkably informative artifact and can be read as a partial index of a given individual's life. Depending upon the condition of the bones and the methodologies available, archaeologists can answer important questions regarding diet, pathology, migration, cultural affinity, origins, occupation, and a suite of other metabolized traces of culture. When contextualized within an associated archaeological assemblage, human remains can be among the most descriptive, data-rich materials one is likely to excavate (Larsen 2004).

Trace element analyses have become increasingly popular among archaeologists interested in osteology and what it can reveal. Gross anthropometry and anthroposcopy are necessary evaluations, but sometimes the elemental constituents of human bone can be more instructive. Barium, carbon, and nitrogen, for example, have been extensively studied in pursuit of past dietary strategies and the environmental and social shifts which influence them (Larsen 2004:270-296; Keegan and DeNiro 1988). Pathological conditions might be assessed by looking for toxic concentrations of mercury and arsenic, or by studying deficiencies of essential metals like iron (e.g. Rasmussen *et al.* 2008; Oakberg *et al.* 2000).

Strontium isotopes collected from teeth and bones can be compared to suggest human migration patterns in the distant past (e.g. Bentley 2006). The chemistry of human physiology encrypts certain practices which archaeologists might otherwise be unable to synthesize or substantiate.

One element which has proven particularly versatile for archaeological research is lead. The metal itself is toxic in very small quantities, serves no known biological function, but due to its long and widespread history in materials manufacture, has become one of the most bioavailable toxins in the world. Lead acquired during life can enter the body through food, drink, occupational exposure, and a myriad of other culturally-facilitated pathways. With a high affinity for bone, metabolic lead takes up residence in the skeleton, becoming a quasi-permanent fixture and remobilizing only very slowly during an individual's life. What remains of this lead burden after death becomes the subject of archaeological chemistry, and the results of scientific analyses can be very illuminating (e.g. Aufderheide 1985; Carlson 1996; Bower 2005).

Proper assay of skeletal lead's elemental and isotopic profiles can disclose information about diet, occupation, pathologies, migrations, cultural affiliations, and a variety of social behaviors. But archaeologists must be careful, as many lead-in-bone studies come as a cautionary tale. Many factors associated with the burial environment can alter antemortem lead levels, and if these are not meticulously considered, archaeological conclusions can be jeopardized. Furthermore, chemical data recovered from remains for which postdepositional changes have been well characterized must not be considered as sole lines of evidence (or somehow better because they are scientific). Results must always be contextualized and considered along with other, equally valid kinds of information, lest conclusions become distorted.

With this in mind, this paper seeks to explain lead's importance to the archaeological study of human bone. In one sense, this has been undertaken to demonstrate how the proven caliber of chemical analyses can be coupled with the rich interpretive powers of archaeology to produce an admirable and ambitious discipline. And yet in another sense, this paper has been written to characterize the successful execution of such analyses, not only by providing information relevant to methodological considerations, but by underscoring how these methodologies can be (and have been) used and misused.

This paper has been divided into five chapters, each comprising a series of related topics necessary to the analysis of lead in archaeological bone. Chapter 1 provides an overview of lead's physical characteristics, together with a summary of its clinical toxicology and toxicokinetics. It is important to

understand how the metal interacts with human biology, including the temporary and permanent influences it may exert, in order to understand why its measurement is important to archaeologists. In Chapter 2, lead derived from anthropogenic sources is discussed in terms of its role in industry and materiality, how it cycles in an ecosystem, and how lead deposited after burial may affect human remains through diagenesis. Chapter 3 addresses a wide variety of scientific methodologies available for the study of lead in bone, and discusses the operation of each, as well as their respective advantages and limitations. Chapter 4 outlines a historiography of archaeological lead-in-bone studies, mostly within the purview of historical archaeology (North American/Caribbean post-contact) but inclusive of other contexts where these are deemed instructive. And Chapter 5 consists of a case study which demonstrates how a proper methodological program ought to be implemented, and how this can be applied to a novel archaeological question.

It is the hope and intention of this paper to make the lead found in archaeological bone of key analytical concern for bioarchaeologists. The versatility of lead lies in the diverse information it can encode for a given individual. It is rare in archaeology to have a single analyte be able to proffer so much potential data, and if great care is taken in its analysis, lead's contributions to archaeological understandings can be inestimable.

CHAPTER 1

The Nature of Lead: Elemental Characteristics and Toxicity

BASIC CHARACTERISTICS

Lead (Pb) is a member of group 14 as classified by the periodic table, sharing this status with carbon, silicon, germanium, tin, and ununquadium. It has an atomic number of 82, with a standard atomic weight of 207.19. Four stable isotopes of lead exist naturally, three of which are the products of radioactive decay (^{206}Pb from uranium, ^{207}Pb from actinium, and ^{208}Pb from thorium), while the other, ^{204}Pb , is nonradiogenic (Skerfving and Bergdahl 2007:600; United States Department of Health and Human Services [USDHHS] 2007:277). The natural ratios of these isotopes are not fixed, but instead depend wholly on the geological processes. All isotopes possess six electron shells of 2, 8, 18, 32, 18, and 4 electrons per shell.

The metal itself is relatively heavy, with a bluish-grey hue. Its physical properties most relevant to human industry and technology are its ease of malleability, high ductility, relative softness, poor electrical conductivity, low melting point (621.43°F), and its high resistance to corrosion products (lead sulfates, oxides, and carbonates will form on its surface whenever the pure metal is exposed to air or water; USDHHS 2007:277). Taken together, these characteristics have made the extraction and smelting of lead an attractive pursuit for numerous cultures across a wide variety of spatial and temporal contexts (see Chapter 2).

Lead, however, is not a particularly abundant element on earth, and the average concentration in the crust is on the order of 13mg/kg (Bjerregaard and Andersen 2007:268). This leaves the average global accumulation near the surface, in a natural state (i.e. one not modified by anthropogenic pollution), at approximately 16 $\mu\text{g/g}$, although many modern soils have concentrations between 10 and 67 $\mu\text{g/g}$ (Tucker 1972:88; De Muynck *et al.* 2008:480). Because it exists in such low quantities, lead is seldom encountered naturally as a pure metal. Instead, lead is typically found in sulfide (galena), oxide, or carbonate ores (anglesite, cerussite), and even in these cases, the “average lead content of mined ores ranges from 3 to 8%” (Goyer and Chisolm 1972:57; Rizescu and Cirstea 2008:56).

However, these relatively small ore quantities have not inhibited either historic or modern mining operations. Rare though the metal may be, the ore deposits which contain lead are easily accessible and

feature a wide geographic distribution (USDHHS 2007:277). This has facilitated the development of industries and technologies which take advantage of lead's unique physical properties, but these applications come at a price. Anthropogenic lead has grossly contaminated much of the globe, especially those areas where it is most heavily processed, leading to significant environmental contamination (see Chapter 2). Lead materials, industry, and environmental pollution, have made the metal one of the most highly distributed toxins in the world.

TOXICOLOGY

Lead does not serve any known biological function for humans, instead causing a variety of deleterious pathologies ranging from very mild bodily pains to neurological damage to death. As a broad-spectrum toxin, lead can harm an array of biological systems, provided that it is acquired in dangerous enough quantities.

Most clinical studies report that normal background Pb blood levels in non-occupationally exposed adults are on the order of 5 to 15 μ g/100ml, while young children ideally have concentrations below 10 μ g/100ml of blood. Typical daily intake for modern adults ranges from 20 to 200 μ gPb/day, and once ingested, the metal can be detected in a wide variety of biological media (bone, blood, urine, feces, hair, sweat, nails, breast milk, and saliva). Biomonitoring lead in the human body is therefore facilitated by its omnipresence in biological tissues and fluids, which has allowed clinicians to characterize the toxicokinetics of Pb fairly well (Winder *et al.* 1997:132).

A long history of technological use, combined with common modern applications (paint pigments and antiknock gasoline additives), have made lead exposure in industrialized countries a key concern of national and international health programs. Given the numerous opportunities for occupational and environmental exposure, it should be no great surprise that lead is, quite simply, "the most extensively studied of all toxic agents" (Skerfving and Bergdahl 2007:599).

Lead's toxic effects are broad, as the metal interacts with a multitude of tissues and systems. Hematological, osteological, cardiovascular, gastrointestinal, reproductive, neurological (central and peripheral), and renal systems are variously affected by different concentrations of acquired lead. Both

physiological and behavioral pathologies may result from excessive lead intake. Table 1.1 summarizes some of the more prevalent of these.

Biological Site/System	Toxicological Effects
Blood	Decreased heme biosynthesis Anemia
Kidney	Vitamin D ₃ impairment Gout Renal failure
Cardiovascular	Hypertension Cardiac conduction impairment Cardiac calcium influx ECG abnormalities Increased arrhythmias
Bone	Adverse dental development Delayed skeletal maturation Decreased plasma osteocalcin
Central Nervous System	Memory loss Learning difficulties Visual impairment Functional deficits Encephalopathy Edema Seizure
Reproductive System	Spontaneous abortion Adverse sperm morphology Impaired sperm count
Gastrointestinal	Colic Constipation Severe abdominal pain

Table 1.1 – Adapted from Medeiros *et al.* 1997:171 with additions from Landrigan 1990:62, Miller and Groziak 1997:378; Bodin and Cheinisse 1970:115; Borja-Aburto *et al.* 1999.

Table 1.1 is not all-inclusive, and a few other symptoms indicative of high lead levels are important to mention. These include general weakness, paralysis of the fingers, sleep disturbances, aggressive behavior, and hyperactivity (Miller and Groziak 1997:378; Bodin and Cheinisse 1970:115). In addition to these large scale effects, lead can adversely influence subcellular systems as well. Chromosomal damage from lead exposure can be so acute that breaks may occur within their structure, fragmenting them within a given cell. Mitochondria, the organelles responsible for cellular energy production, may have their metabolic functions impaired, leading to cellular death. In addition to metabolic impairment, the mitochondria's detoxification abilities may also become severely compromised (Fowler 1978:37-38; Nordberg *et al.* 2007:133-134; a more detailed study of DNA lead toxicity can be found in Popenoe and Schmaeler 1979). Clinical research also suggests that lead may promote the growth of certain tumors, and its carcinogenicity has been evaluated in both human and non-human animal models (Ke *et al.* 2007).

It should be noted that varying concentrations of lead in the body will result in the expression of different pathologies, some of which can begin to manifest with as little as 10 to 20 $\mu\text{gPb}/100\text{ml}$ blood (enzymatic inhibition in haem and porphyrin biosynthetic pathways; Winder *et al.* 1997:132). Though these minor amounts certainly distress some biological systems, clinical lead poisoning is generally considered to occur when blood concentrations exceed 40 $\mu\text{gPb}/100\text{ml}$ (Hu and Hernandez-Avila 2002:1088).

However, gross blood-lead concentration is not solely dependent upon gross lead intake. Other biophysical factors will influence how much lead is absorbed, and no single factor alone dictates pathological severity. The metabolism of other metals, for example, plays a significant role. Because lead and certain other divalent metal ions compete for physiological absorption (particularly calcium, a biological analogue to lead), certain symptoms can be mediated or exacerbated depending upon the biophysical occurrence of these ions. For example, low levels of calcium will likely increase the risk lead intake poses to various organs. Iron deficiencies will also allow for greater quantities of lead to be absorbed, increasing the susceptibility to lead poisoning (Medeiros *et al.* 1997:171).

TOXICOKINETICS

Toxicokinetic models depicting how lead enters and circulates throughout the body abound in the clinical literature (see, for example, O'Flaherty 1993; Rabinowitz *et al.* 1991; Rosen and Pounds 1989; Pounds *et al.* 1991; USDHHS 2007:175-202). Though its interactions with different tissues are complex and highly specific, lead is generally acquired metabolically through at least one of three pathways: inhalation, gastrointestinal absorption, or dermal contact. The first two provide the most effective means for lead's metabolic circulation. Absorption through the skin is minimal, and only organic lead (tetramethyl, tetraethyl, triethyl) poses a real threat via skin contact. However, because the most common form of organic lead is the antiknock agent in leaded gasoline (tetramethyl or tetraethyl lead), this route of exposure is far less common today than it had been 30 years ago. Furthermore, because organic lead is metabolized into inorganic lead in biological systems, toxicokinetic models seldom address organic lead (USDHHS 2007:6-7, 35, 166; Skerfving and Bergdahl 2007:633).

Inhalation can be a major route of exposure, as lead aerosols created during industrial processing can be carried great distances in enormous quantities (see Chapter 2). When inorganic lead is inhaled, most

of the submicron particles are absorbed through bronchiolar and alveolar tissues (though the majority of this lead will ultimately be excreted). Particles larger than one micron will typically be cleared from the respiratory system into the gastrointestinal tract (USDHHS 2007:174). It is difficult to estimate how much of an inhaled quantity will be absorbed, as this will depend on the physicochemical properties of the lead itself (such as particle size), as well as a given individual's physiology (USDHHS 2007:156-157).

Gastrointestinal absorption (primarily through the duodenum) is by far the most common and most effective means of lead intake. However, the amounts of ingested lead which are actually introduced into the body through the gastrointestinal tract are relatively small, but are modified by fasting and age. In adults, the average absorption rate has been estimated to be between 6% and 20%, but most adults will absorb somewhere around 10%. (USDHHS 2007:; Gustavsson and Gerhardsson 2005:492; Philip and Gerson 1994:435). However, this assumes an individual is following a regular dietary program. After fasting for just one day, the rate of absorption can climb as high as 60-80% (USDHHS 2007:7). Continuous fasting leading to calcium and iron deficiencies will exacerbate lead's absorption rate and its overall toxicity.

Children are far more susceptible to lead poisoning, as developing physiologies much more readily absorb the metal once it is ingested. Whereas adults will take up 10% of the total ingested lead, children will generally absorb 30-40% (Gustavsson and Gerhardsson 2005:492). It follows that for children and adults occupying the same lead environment, children will almost always exhibit greater levels of the toxin (see Barry 1981:70 for an exception).

Once the lead has been absorbed, it generally follows the same pathways irrespective of age. Upon introduction to the body, lead is highly mobile but slow to transfer from the circulatory system to soft tissues. While in circulation, nearly 99% of blood lead is found in red blood cells, bound to hematic proteins. The remaining lead in the bloodstream is either bound to plasma proteins and globulins, or exists as serum complexes. After four to six weeks in circulation, lead will begin to accrue in soft tissues. Major early sites of deposition include the "kidney, liver, brain, renal cortex, and aorta," although a host of other organ, muscular, vascular, fatty, and cartilaginous tissues will eventually be affected (USDHHS 2007:169; Philip and Gerson 1994:436-437; Barry 1975:121). The actual amount of lead which reaches these areas is dependent on a suite of highly particularized characteristics, but Barry (1975:121) found that non-

occupationally exposed adults generally exhibited lead levels below 1µg/1g (1 part per million) in these soft tissues.

Bones accumulate lead to a greater degree than any other part of the body. Several weeks after ingestion, most of the lead retained by the body (99% or so will have been excreted) will take up residence in the skeleton. Approximately 94% of lead retained in adults, and 73% in children, will be stored in the bone mineral, hydroxyapatite (USDHHS 2007:7-8). Because lead competes with calcium for a variety of biophysical processes, it is suggested that the metal replaces some of the calcium in bone. Lead ions form “highly stable complexes with phosphate,” and therefore may substitute for Ca in the calcium-phosphate salt which comprises the crystalline minerals of inorganic bone (USDHHS 2007:205; Coon *et al.* 2006:1872). Interestingly, the metal is not deposited uniformly throughout the skeleton, and different bones within the same individual can vary significantly in terms of lead concentrations (see Barry 1975:121-122). The dense matrix of cortical bone tends to store more lead, whereas the spongy structure of trabecular bone will more readily exchange with blood.

Lead’s distribution within a given bone may not be uniform. Some studies have found that lead tends to accumulate at the periosteal and endosteal surfaces during life, diminishing in concentration toward the center of cortical bone (human model, Todd *et al.* 2001; non-human animal model, Bellis *et al.* 2008). In contrast, Wittmers *et al.*’s 2008 study of lead’s microdistribution in archaeological bone revealed that while lead may concentrate at bone surfaces in some cases, in others the metal’s distribution is highly irregular. Therefore, while lead may sometimes pool toward superficial bone regions, the depositional processes cannot be generalized. But the distinction between lead at the surfaces and lead toward the interior may be important, not for reasons of microdistribution but for lead’s kinetic behavior at these sites.

Lead deposited in bone occupies one of two physiological compartments. In one compartment, the metal is available for remobilization from the bone back into the circulatory system, where it proceeds to other tissues, becomes deposited in bone again, or is excreted from the body entirely (USDHHS 2007:169-170; Smith *et al.* 1996:60; Coon *et al.* 2006:1872). Normal bone metabolism requires regular bone turnover (the rate of apposition/resorption, or the mass of calcium exchanged) in order to maintain homeostasis. Adult trabecular bone has a 32% annual turnover rate, whereas cortical bone’s turnover is around 4.3% per year (Carvalho *et al.* 2004:1251). Metabolic remodeling will therefore remobilize lead from trabecular bone

much more readily than from cortical tissues. This process may begin after a fairly brief residence time in bone, perhaps on the order of 100-200 days following initial introduction to the body (Marcus 1985:441).

Other physiological processes which affect bone turnover rates will also affect how much lead is leached into the bloodstream. For example, during pregnancy, lactation, menopause, and osteoporosis, a considerable amount of lead can be remobilized due to accelerated bone demineralization during these physically stressful periods. In some cases, enough lead is mobilized that an individual's skeleton can actually represent an endogenous source of low-to-moderate lead exposure (Machida *et al.* 2009:880, 884-885; Berglund *et al.* 2000:221; Theppeang *et al.* 2008:784).

The other physiological compartment that bone lead can occupy is a relatively inert one. Most of the lead which enters the inorganic skeletal matrix is bound there for a long time, and is referred to as an individual's overall lead burden. Lead's half-life in cortical bone is approximately 20 years, while in trabecular bone lead will have a half-life of around 10 years (compare this to blood lead's half-life of roughly 30 days; Hu *et al.* 1998:1; Coon *et al.* 2006:1872; Park *et al.* 2009:1422). Therefore, lead found in bone represents long-term exposure, as opposed to chronic, acute exposures which would be better characterized by blood lead levels.

Thus bone lead indicates lifetime intake, and is roughly a function of age in non-occupationally exposed individuals. While children will generally show higher lead values than adults from the same lead environment, this is due to their much higher rates of bone formation. However, this high bone activity will eventually expel much of the lead from their skeletons, provided exposure is not chronic. As children approach adolescence and bone formation gradually slows, lead levels will likely drop, thereafter accumulating very slowly throughout adulthood. In older age, levels may again decline due to the demineralization associated with diseases such as osteoporosis (USDHHS 2007:170).

It should therefore be readily apparent that any individual at any stage of life is at risk for Pb poisoning. An enormous variety of media transport lead from exogenous sources into the human body, and may include air, food, water, soil, dust, and technological materials or processes that incorporate any amount of the metal (Pounds and Leggett 1998:1505). Particularly given the modern industrialized society in which many of us live, it should come as no surprise that, on average, modern humans store approximately 100 times more lead in their bodies than peoples from preindustrial settings would have

(Shukla and Leland 1973:1320). The contrast is a stark one that warns us to be mindful of lead's several hazards. The following chapter will discuss the materiality of lead toxicity, the means by which the metal became so broadly dispersed, and how humans might still acquire it postmortem.

CHAPTER 2

Anthropological Lead: Materiality, Biogeochemistry, and Diagenesis

The processes which contribute lead to a human skeleton can be divided into two categories, separated according to a simple, but absolutely integral distinction: when, relative to death, was the metal acquired? On the one hand, lead which accumulated during a person's life is tied very closely to particular cultural practices in which that individual participated. On the other, lead which is derived from the burial environment is indicative of biogeochemical processes, and does not speak to the sorts of anthropological questions archaeologists seek to answer. Thus, it is imperative to distinguish between antemortem and postmortem lead uptake if biological levels are required for a given research design, lest the data be unreliable. The methods for discriminating between metabolic and diagenetic lead are discussed in Chapter 3, but a deeper understanding of how lead is culturally and geologically acquired is essential to characterizing lead in bone. This chapter will therefore briefly address some of the more common cultural sources of lead exposure before moving to discuss lead's interaction with soils and its uptake from the burial environment.

LEAD AND CULTURAL MATERIALITY

Because lead is relatively easy to work with and its deposits are fairly widespread, its incorporation into an enormous variety of material culture should come as no surprise. Physical qualities such as high malleability and ductility, corrosion resistance, and a low melting point have made lead an ideal candidate for numerous technological purposes. Industrial enterprises designed to extract and exploit the versatile metal have endured for millennia, the archaeological evidence for which extends back at least 7000-8000 years (Liu *et al.* 2007:943; Lambert 1997:174). Geographically, lead manufacture is ubiquitous, with industrial processing evident on every continent except Antarctica. Worldwide mining operations extract nearly 3 million metric tons of lead, the majority of which comes from China, Australia, the United States, and Peru. Together with the amount recycled every year, worldwide production is more than twice that figure (Skerfving and Bergdahl 2007:602).

Among its more popular modern uses, lead has featured as a gasoline antiknock agent, a component in batteries, a paint pigment, ammunition, plumbing, cable sheeting, solder, pesticides, and

innumerable chemical compounds (Philip and Gerson 1994:423; Shukla and Leland 1973:1320-1321). It would be a futile attempt to specifically address the myriad products in which lead has been incorporated. However, a brief description of some salient archaeological examples, with a strong focus on those in the context of historical archaeology, will suffice to demonstrate its timeless utility.

Ancient civilizations of the Mediterranean used lead in plumbing, glass making, coinage, cosmetics, pharmaceuticals, as well as numerous foods (such as the Roman fish paste *garum*) and beverages (“sugar of lead,” i.e. lead acetate, was used to sweeten wine; Shotyk and Le Roux 2005:247; Eubank 1996:46). In metallurgy, lead’s co-occurrence with silver in many ores made its extraction an economically enthusiastic enterprise, while its use in bronze alloys facilitated casting (Lambert 1997:186-187, 206).

Lead has been a common ingredient in the production of certain kinds of glass for centuries. The addition of lead oxide lowers the melting point of silica, can add a brilliance or fine opacity to glass, and can contribute beautiful coloration when various forms and quantities are added. Lead glass has been historically produced in China, Japan, the Islamic world, the Roman Empire, and throughout pre-Roman European civilizations. Modern lead crystal, a popular form of glassware (it is in fact glass, not crystal), was created by George Ravenscroft of England in 1674 and exhibits a striking brilliance owing to its high lead content (Lambert 1997:127).

For historic archaeologists interested in the lead content of archaeological bone, two artifact categories represent the most likely reservoirs of bioavailable lead: pewter and ceramics. Pewter, a tin alloy typically containing between 5 and 25% lead, was often used for utensils and serving vessels among the economically advantaged (Lambert 1997:187; Wittmers *et al.* 2008:671). Acidic foods or beverages stored, prepared, or served in these containers had the potential to leach lead from the objects, contaminate the comestible, and poison the consumer. Social correlations between archaeological skeletal lead burdens and the use of pewter wares have been investigated, and will be discussed in detail in Chapter 4.

Ceramics comprise the other major source for lead contamination in the context of historical archaeology. Lead has been used for millennia as a key element in certain pottery glazes. The metal acts as an ideal fluxing agent, helps to mitigate the shrinking during production, and gives a smooth, appealing shine to the pottery body (Lambert 1997:60). But while it might be ideal for use in the production of

silicate vessels, any acidic liquid contained within the final product can very easily leach lead from the glaze. As with pewter, any foodstuffs contained, prepared, or presented in lead-glazed pottery can potentially poison the provisions and the person enjoying them.

Leaden pottery has a long history, particularly in the West and Middle East where it appears in one of two predominant forms: transparent high lead glazes and tin-opacified glazes. These have been commercially available for at least 1000 years and could poison anyone who could afford them (Tite *et al.* 1998:242). With regard to the specific types of lead-leaching pottery one could find on a North American historic archaeological site, Eubanks (1996:16-27) tested a large variety of ceramics available to colonial and national Americans. Her findings indicate that at least some shards from the following ceramics leached lead under experimental conditions: glazed redware, yellow/brown decorated buff slipware (ca. 1670-1795), creamware (ca. 1762-1820), a variety of pearlware (ca. 1780-1890), glazed whiteware (ca. 1820), some hardpaste porcelains (ca. 1885), delftware (ca. 1680-1800), and Whieldon ware (ca. 1740-1770). The examples Eubanks tested have a wide range of economic values, suggesting that lead exposure via toxic ceramics would have been potentially available to persons from a wide range of social classes.

Today, most of the lead which we are likely to encounter no longer comes from material reservoirs, but rather the deposition of atmospheric lead in the surrounding environment. Most environmental lead contamination is a direct result of human activity. While it is true that the natural world circulates lead according to ecologic and geologic processes such as volcanism (~ 20-40% of atmospheric lead), glacial activity, tectonics, fires, and floods, human industry has “considerably accelerated the process of lead redistribution” (Shukla and Leland 1973:1320; Nriagu 1989:48). Lead concentrations taken from polar ice cores indicate a 200-fold increase in atmospheric lead accumulation over the past three millennia, worsening during the second half of the 20th century by the use of lead gasoline (Philip and Gerson 1994:425). Interestingly enough, the lead modern humans continuously pump into the atmosphere or directly into local environments can still contaminate archaeological populations through a process known as diagenetic uptake. In order to properly understand how modern lead can intoxicate past peoples, a rudimentary knowledge of how lead interacts with soils is required.

BIOGEOCHEMICAL CYCLING OF LEAD - DEPOSITION

Ecological cycling of lead is a fairly complex process, subject to both regional and highly localized biogeochemical processes. Interactions with sediments and soil solutions will determine the mobility of lead, a phenomenon of critical importance to any study of archaeological bone that needs to assess what effects the burial environment has on skeletal materials. This is certainly necessary in the case of most trace element analyses, and has proven paramount for studies of lead in bone. In order to address questions of postmortem uptake, one must first cultivate a general understanding of lead's depositional and mobilization parameters.

The remainder of this chapter will primarily address lead as it occurs in soils, although lead in marine burial environments can be of equal importance, and its aquatic cycling is well researched (e.g. White and Driscoll 1985; Kalnejais *et al.* 2003; Rippey *et al.* 2004; Blais and Kalff 1993). It would, however, be beyond the scope of this paper to address every environment in particular, and because most burials occur on land, these are the most relevant to archaeology.

The exact quantities of anthropogenic lead introduced into the biosphere are difficult to precisely quantify, but environmental contamination has reached "orders of magnitude above natural levels" (Smith and Flegal 1995:21). Industrial and technological practices have always been the prime movers of lead, but their acceleration in recent historical trends are responsible for the inordinately high environmental concentrations of lead. The European and American industrial revolutions have discharged more than 300 million metric tons of lead into the biosphere over the past three centuries (half of the estimated total lead production). However, the most effective means of lead dispersal came with the advent of alkyl-lead gasoline additives which, while used since the 1920s in the U.S., became heavily combusted worldwide during the 1970s. The burning of leaded gasoline "prior to regulation, became the single most significant source of global lead emissions to the atmosphere" (Smith and Flegal 1995:21; Lazarus 1970).

Most lead fallout does not migrate more than a few miles from its point of production, but lead particulates discharged into the atmosphere can travel thousands of miles across international boundaries to contaminate areas that would otherwise be unpolluted. Polar ice strata, Greenland snows, and even deep sea sediments are all isolated environments which anthropogenic lead has permeated (Murozumi *et al.* 1969; Patterson 1987:244-245; Boutron *et al.* 1991; Rosman *et al.* 1993). The extent of contamination is not

uniform, however, as dispersal patterns are regionally-based and tend to concentrate most heavily in urban environments. But the fact remains that far reaching areas of the global ecosystem are significantly affected by industrial lead, and thus *any* archaeological environment has been potentially contaminated. In fact, human dispersal is so great that it is estimated “that more than 95% of lead now within the biosphere is of anthropogenic origin” (Smith and Flegal 1995:21-22).

Atmospheric lead is the primary source of broad-scale deposition. As mentioned, leaded gasoline has contributed enormously to levels of atmospheric lead, but any process which emits volatile lead compounds can disperse the metal atmospherically. Lead sorbed onto aerosol particulates can become circulated into the upper troposphere and transported hundreds, if not thousands of miles during its 7- to 14-day residence time by meteorological forces (Miller and Friedland 1994:662). The metal particles will then precipitate with water, depositing in ice, snows, marine sediments, terrestrial soils, and waterways. This process is generalized, and the extent of a site’s pollution seems to be a function of its proximity to production sources and certain meteorological/geographical determinants. For example, in the eastern U.S., lead is deposited from the atmosphere via rainfall at lower elevations and cloudwater (e.g. fog) at higher altitudes. Because both rainfall and cloudwater increase relative to elevation, sites situated at higher altitudes are eligible for higher degrees of contamination. But characterizing deposition patterns for a given area will depend on sources for atmospheric lead, local topography, and weather activities and must be assessed on a case-by-case basis.

BIOGEOCHEMICAL CYCLING OF LEAD - SOIL MOBILITY

The relative mobility of Pb in soils will depend primarily on local biogeochemical processes at work, both historically and presently. Prevailing chemical activity in a recently excavated burial environment cannot be assumed to characterize the entire site’s chemical history. Local fluxes in temperature, pressure, pH, organic activity, and so forth must be expected to have occurred over time. This is relevant to discussions of bone’s diagenetic modification, and needs to be considered in the assessment of any burial environment. The following is a discussion of how lead might interact with soils in general, with particular attention given to studies of the eastern/northeastern forests of the United States (from which the case study in Chapter 5 is derived).

Once lead is deposited on local soils, its kinetics will be determined wholly by certain biological, chemical, and thermodynamic variables. Most of the lead which is taken up by forest soils remains within the biologically active humic layer overlaying the mineral subsoil. Studies of U.S. eastern and northeastern ecosystems suggest that perhaps as much as 70% of anthropogenically deposited lead is retained in the surface soils (Van Hook *et al.* 1977:285-286; Wang and Benoit 1996:2211; Johnson *et al.* 1995:813). Concentrations in the northeastern U.S. can range from between 90 and 225mg/kg in organic soils. Pooled in the organic horizon, lead will decrease to 37% of its original amount after 50-150 years in North American forests, and be completely cycled in 150-500 years (Klaminder *et al.* 2006:32; Friedland *et al.* 1992:400). What becomes of the vanishing lead is a matter of some concern to archaeologists.

Most of the lead will not be incorporated into local ecosystems, as the metal has no nutritional benefit to plants and does not typically leach into aquatic ecosystems from soil environments (Johnson *et al.* 1995:816; Van Hook *et al.* 1977:286; Wang *et al.* 1995). Instead, lead can concentrate in the mineral soils lying below forest floors. How it is mobilized is a highly particularized process, but some general characteristics can be given.

Lead is not normally soluble, but can bind with a variety of particulates in the soil (colloids) which will facilitate its mobility in the right chemical media (soil solution). Lead has a particular affinity for organic materials dissolved in humic acids from overlying vegetable matter. Dissolved macromolecules, bacterial polymers, biological debris, and microorganisms originating in the organic horizon may bind with Pb and transport it downward into soil substrata. Inorganic soil matter can also complex with lead and introduce it into deeper layers. Certain clays can carry lead, as well as other colloidal metals such as aluminum or iron sesquioxides and calcium carbonate (Bergkvist *et al.* 1989:264; Chen *et al.* 1995:53; Michopoulos *et al.* 2005:354; McCarthy and Zachara 1989).

Lead mobilization is dependent not only on chemical interactions with local materials, but also the soil solutions of the local environment. In general, lead is more readily transported in acidic soils (due to the increased availability of the particles with which it binds), although highly alkaline soils can accomplish this as well (Bergkvist *et al.* 1989:277; Wang and Benoit 1996:2218). Higher temperatures and increases in soil moisture content can also leach lead from the humic layer into deeper profiles (Tyler 1981). Other factors which will influence lead's mobility are seasonal precipitation, soil disturbances and

turbation (mixing), local cation/anion inputs, site history, and site location (Steinnes and Friedland 2005:293).

It is difficult to say how much lead will leach downward, how fast, and to what depths. One study of an Ontarian woodland indicated that >99% of soil lead migrated into the mineral soil, the majority of which (85%) was located between 0 and 10cm (Watmough *et al.* 2004:59). In general, for podzols and brown forest soils (common to many temperate areas), most of the lead will accumulate in the upper part of the mineral soils horizon (B Horizon), the depth of which is determined by local geology.

Because lead-soil interactions are dependent on specific physicochemical attributes, individual sites need to be characterized for the extent of their Pb pollution. This is important for environmental health studies, but its necessity for bioarchaeology has been increasingly acknowledged. Because post-depositional trace elements can invade buried bone, antemortem levels can be severely distorted. This is a phenomenon of diagenesis, and is the subject of this chapter's final section.

DIAGENESIS – POSTMORTEM SKELETAL UPTAKE OF LEAD

Diagenesis is a subcategory of taphonomy, the study of those processes which modify organic matter after death. Diagenesis, therefore, has often been conceptualized as research that has a strict organic focus, but postdepositional modification is relevant to any archaeological material, and must be more broadly conceptualized. The definition offered by Wilson and Pollard (2002:644) was conceived in such a way:

“Diagenesis is...the cumulative physical, chemical, and biological processes that alter all archaeological materials in the burial environment and is consequently a fundamental characteristic of the archaeological record. These processes will modify an inorganic object's original chemical and/or structural properties and will govern its ultimate fate, in terms of preservation or destruction.”

The processes of post-depositional change alter an object until it is in a state of equilibrium with its environment, at which point it stabilizes (thermodynamically speaking). However, the conditions of most burial environments are not constant, and thus most artifacts never truly stabilize. The flux of local and regional biogeochemical processes will continuously alter most archaeological materials, rendering them in different physical states throughout their diagenetic histories. More often than not, diagenesis tends toward the deterioration of an artifact's original state, but under specific (although rare) circumstances, diagenesis

may ultimately preserve buried cultural materials (Wilson and Pollard 2002:644-645). Post-depositional dynamics, though, are also important in terms of their processes, not just their outcomes, because they shed light on a given object's burial history. With specific regard for bone, R.E.M. Hedges reminds us that,

“bone is not only a complex material, but it contains information at many different levels (isotopic, molecular, biochemical, and structural), of which any type can be of engrossing concern in research. So diagenetic studies not only have to deal with the processes that change the nature of bone during burial, and how these processes are environmentally determined, but also the ways in which specific types of embodied information are altered or recovered” (Hedges 2002:319).

Archaeological literature on bone diagenesis is massive, and many studies of postmortem lead uptake are available (for other trace elements see Nelson and Sauer 1984; Millard and Hedges 1995, 1996; Pike and Richards 2002). The past three decades have witnessed an analytical trend which has sought to better characterize how soil lead might affect buried bone. Its two major lessons for archaeologists have been that diagenetic lead uptake is 1) a highly complex process which remains incompletely understood, and 2) a variable which all bioarchaeological studies of lead must consider.

It is methodologically sound to assume that diagenetic uptake has occurred to some degree. Many soils contain lead in the range of 10-67 parts per million (ppm), and as the sections above demonstrate, some of it will more than likely be available for transport into deeper strata (De Muynck *et al.* 2008:480). Thermodynamic and chemical processes which make lead available for transport likewise enable its migration into buried skeletal remains. Microorganisms, soil solution chemistry, local soil metal ions, bone histological integrity, temperature, and hydrology will all play a role in whether the metal infiltrates a skeleton and the degree to which it has occurred.

Bone's preservation is compromised by some of the same conditions which facilitate lead transport (acidic pH and microbial activity, for example). Bone undergoes recrystallization (replacement of the original mineral crystals with larger ones) below neutral pH, which can increase its porosity and enable more lead to accumulate in its interior (Berna *et al.* 2004:880). Microbes can severely damage bone, and their invasions can likewise transport metals beyond the skeleton's peripheral surfaces (Jans *et al.* 2004; Grupe and Piepenbrink 1989). Percolating groundwater, however, is the primary conveyor of lead-complexing colloids to buried remains, and is responsible for introducing most of the diagenetic lead to the skeleton. There is some uncertainty as to whether the Pb ions which migrate to the bones actually undergo heterionic exchange with calcium, or if the lead is simply deposited in voids within the bone crystal.

Laboratory experiments in neutral and acidic pH indicate the latter, but regardless of its precise mechanism, diagenetic uptake has the capacity to contribute a multitude of exogenous ions to the skeleton (Wittmers *et al.* 2008; Lambert *et al.* 1985:91).

As noted above, there is some uncertainty as to the distribution of lead within a bone. While it is known that trabecular bone is highly susceptible to soil lead uptake, the actual patterns of deposition within cortical bone have been put into question (Carvalho *et al.* 2004:1255-1256). Many researchers have long believed that by removing a 1mm cortex from the periosteal and endosteal surfaces of cortical bone prior to chemical analysis, most diagenetic lead could be effectively removed (Ericson *et al.* 1991:219). But due to the unique histological architecture of every person's skeletal anatomy, lead may be distributed with a high degree of variability between samples (this variability has been observed both ante- and postmortem; see Wittmers *et al.* 2002:674). It seems likely that the most superficial tissues (at the periosteal and endosteal surfaces) will be compromised first, but naturally occurring or taphonomic spaces within the bone would also be eligible for contamination (Wittmers *et al.* 2008:385). Furthermore, too many variables dictate the depth of lead's penetration, and generalized diagenetic programs are therefore difficult to formulate. While some researchers have attempted to develop broadly-conceived diagenetic trajectories (e.g. Smith *et al.* 2007), these will have to be modified to such a degree at each local site that their utility seems undermined.

Before any lead analysis data can be interpreted, some attempt to address the diagenetic component of bone must be undertaken; it is critical not to make simple assumptions without empirically testing them. Early studies of lead in bone assumed that if the gross lead levels in the burial soils were significantly less than those in the bones, then diagenesis could not be too severe. This has since been challenged, as over time, even limited quantities of soil lead ions can accumulate to a high degree in bones (Wittmers *et al.* 2008).

One way to test for the presence of diagenetic lead would be to test skeletal samples for elements common in the surrounding soils but relatively scarce in living bone. If an atypically high concentration of one of these 'diagenetic markers' is found, one can begin to characterize diagenesis (Buikstra *et al.* 1989:158). Another method might be to immerse bone samples in a sodium acetate buffered solution (pH4.5) to dissolve any hydroxyapatite crystals which have been reconfigured by percolating water. Groundwater ions are soluble at this pH, while antemortem apatite is not (Sillen 1986; Wittmers *et al.*

2002:671). It is assumed that any postmortem ionic contributions would be dissolved, although this procedure is not well documented for lead in archaeological bone and might dissolve some of the antemortem lead. Perhaps the most effective treatment is to quantify the different lead isotopes in soils and bones, and compare their ratios. If the quantities of each ion are significantly different between the burial environment and the skeleton, then diagenetic uptake may only be responsible for a small fraction of the lead in the bone (see Chapters 4 and 5; see also Reinhard and Ghazi 1992; Ghazi *et al.* 1994; Pate and Hutton 1988).

Thus, it is no longer enough to consider diagenesis as a qualitative variable. Instead, the post-depositional changes in skeletal lead burden should be quantified as precisely as possible. The validity of archaeological conclusions is at stake, as many hypotheses which do not take diagenesis into serious consideration might be wrongly supported or rejected.

CHAPTER 3

Lead in Bone: Archaeological Methodologies

Selecting an appropriate methodology is of paramount importance when designing a lead analysis for archaeological bone. One must very carefully consider the advantages and disadvantages of the numerous techniques now available to modern investigations, and how these will ultimately affect the quality of the data needed to answer a given research question. These variables include, but are not limited to, sample condition, selection, and preparation, diagenetic parameters, instrumental sensitivity, analytical versatility, cost, timeframe, materials availability, and the acquisition or creation of standard reference samples. These and other factors will all bring their own requirements to bear, and compromises will certainly need to be made. It is particularly important to understand the differences in raw data between different methodologies, and to select the one best suited to the archaeological problem at hand.

This chapter is included to provide some perspective on many of the procedures used in a variety of archaeological contexts to characterize lead in bone. Limitations, advantages, technological descriptions, and instrumental sequences (for the more common procedures) are provided for the methodologies below, each of which is addressed in its own section. Some of the techniques are well represented in the literature, while others have enjoyed limited (if any) use, but are included to suggest either current potential alternatives or those which may be available to the next generation of archaeologists.

ATOMIC ABSORPTION SPECTROMETRY

Borrowed from analytical chemistry, the most common tests for determining the make-up of archaeological bone rely on techniques which use the visible (and near-visible) regions of the spectrum to quantify elemental composition (Pollard and Heron 2008:19-20). The two procedures which dominate this kind of testing are atomic absorption spectrometry (AAS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Both techniques have been used with great success in archaeology, and their basic principles, advantages, and limitations are discussed below.

Atomic absorption spectrometry was the dominant means for studying lead concentrations in archaeological bone through the 1970s and 1980s. Its relatively mechanical simplicity made it ideal for most archaeological applications seeking single-element quantifications. Atomic absorption spectrometry

replaced an earlier analytical standard, optical emission spectroscopy (OES). This predecessor used an electric spark to volatilize archaeological samples, causing them to emit light. Emissions were focused through a series of lenses onto a prism or diffraction grating, and the wavelengths characteristic of each element under study could be recorded. Many early studies employing OES sought the elemental composition and/or provenance of certain metallurgical and ceramic artifacts, many in the context of antiquity (e.g. Britton and Richards 1969; Atasoy and Buluç 1982; Megaw and Jones 1983; Pollard and Heron 2008:25). Few, if any studies in historic archaeology used OES to quantify elements within the skeleton, most likely because atomic absorption spectrometry was simply a superior technique. However, the basic principles of OES are still employed by many instruments presently in use for lead analysis in human bone.

Atomic absorption spectrometry is a relatively simple tool, and has been used often in the quantification of lead in archaeological human bone (e.g. Jarcho 1964; Mackie 1975; Waldron *et al.* 1976; Waldron 1981). The technology itself takes advantage of one of the most basic principles of atomic electricity using the Bohr model of the atom. This model characterizes atomic structure as a positively charged nucleus surrounded by a ‘cloud’ of orbital electrons with particular energy levels (Pollard and Heron 2008:20; Bohr 1913a, 1913b). Each element, having a unique “nuclear charge and orbital electron configuration,” can therefore “only emit or absorb electromagnetic radiation in fixed units or quanta, corresponding to the energy difference between electron orbitals” (Pollard and Heron 2008:21). The transition of energy between orbitals gives each element a distinct, signature wavelength in the visible light spectrum when excited (Pollard and Heron 2008:21-23). Therefore, each element in the periodic table has a known “line emission or absorption spectrum in the visible region of the spectrum” relative to its orbital electron structure (Pollard and Heron 2008:21).

Atomic absorption spectrometry exploits this basic fact of quantum mechanics through an ingenious procedure that borrows from earlier spectroscopic methodologies (OES in particular; Pollard and Heron 2008:24-25). The following is the general operating procedure for typical AAS analysis.

Samples to be run with AAS must be in a liquid solution to be analyzed. Because the device is typically run as an absorption, light must be passed through the sample in order to determine the elemental quantity under study. This is accomplished using a hollow cathode lamp (glass/quartz envelope containing

an inert gas such as argon or neon at low pressure) whose envelope contains a wire electrode and an electrode resembling a cup containing the element to be analyzed. When a few hundred volts are introduced between these electrodes, the inert gas in the envelope ionizes. The noble gas ions then bombard the cup electrode, exciting the atoms of the analyte element, which then radiates its signature wavelengths (Pollard and Heron 2008:26; Van Loon 1985:23). It should be noted, however, that the hollow-cathode lamp may be unsatisfactory for elements such as lead, in which case an 'electrodeless' discharge lamp can be used to produce the same effect (Van Loon 1985:23).

The lamp light is then guided through the long axis of a specially designed, narrow burner into which the liquid sample is aspirated. Aspiration is achieved via the flow of the pre-mixed, totally homogenized combustion gases, which pulls the sample through a capillary tube into the chamber containing the fuel, and ultimately up into the flame. The fuel chamber has the additional advantage of ensuring that the sample is atomized prior to combustion (Pollard and Heron 2008:26).

Due to the extremely high temperatures of the flame (2200°C for air-acetylene mixtures, 3000°C for oxide-acetylene fuels), "the sample is almost instantly converted into an atomic vapor" (Pollard and Heron 2008:26). Having the sample in this state optimizes the absorption of light from the hollow cathode lamp, the amount of which is proportional to the concentration of the element within that sample. Light passing through the vaporized element shines onto a prism or diffraction grating which divides the beam into its constituent wavelengths. From here, the light passes through a slit which selects for the desired wavelength and transmits the beam onto a photomultiplier detector. This device quantitatively converts light intensity into electric current. The intensity of the light passing through the flame is then compared to a calibration run, which follows all of the same procedures, save for it does so without any sample in the flame. Differences between the two light intensities are used to calculate the elemental concentration in the original, solid sample (sample dissolution affects the sample's weight, and must be corrected for; Pollard and Heron 2008:27).

Newer AAS machines enable the user to run both the calibration and sample beams at the same time by splitting the lamp light with a Maltese cross. This allows one part of the beam to pass through the vaporized sample while the other bypasses the flame altogether. Using the cross has the additional convenience of eliminating the irregularities ('background noise') produced by the flicker of the AAS

flame. Other signal-noise reduction techniques may be employed, and can be found in Ewing 1985 and Van Loon 1985:24-36.

By following careful quality control procedures and optimizing the instrumental conditions, AAS can provide a relatively inexpensive, fast, and reliable analysis of lead in archaeological bone. The detection limits are between 1 and 100ppm (depending upon the conditions of the analysis, the analyte element, and the absorption line used), and has high analytical reproducibility (Pollard and Heron 2008:25). As long as all of the settings are carefully monitored and adjusted, AAS functions well as a tool in archaeological trace metal analyses.

However, it can be difficult to control all of the variables between AAS runs, although computer-controlled instrumentation largely compensates for this. Disadvantages that cannot be controlled to a large extent result from the sequential nature of AAS operation. Atomic absorption spectrometry cannot, in general, satisfactorily quantify multiple elements at once, and must therefore be run numerous times in order to create a composite elemental profile. This can lead to problems in both reproducibility as well as sampling procedure, especially if the sample material is of an extremely limited quantity. Related to this drawback is the fact that unexpected elements in the sample will not be detected, as the device is only set up for the analysis of a particular analyte (Pollard and Heron 2008:28).

One last disadvantage results from the background noise generated by the flame which can interfere with the results (additional signal interferences are given in Van Loon 1985:24-36). While the Maltese cross used in double-beam AAS instruments (see above) helps to eliminate some of these problems, a specific kind of AAS completely removes the primary source of interference—the flame itself (Pollard and Heron 2008:27).

Electrothermal atomic absorption spectrometry (ETAAS) has been used by archaeologists for decades to determine the amount of lead in excavated bones (Aufderheide *et al.* 1981; Aufderheide *et al.* 1985; Corruccini *et al.* 1987; Wittmers *et al.* 2008). This method is similar to traditional AAS, utilizing the lamp, monochromator, and photomultiplier, and even relies on the same basic principles of atomic electricity as described above. The difference, however, lies in the use of a graphite furnace, rather than a flame, to vaporize the sample. Instead of being aspirated in a flame, samples submitted to ETAAS are placed in an electrically heated chamber where they are rapidly atomized in a programmed, easily

controlled, easily repeatable manner (Pollard and Heron 2008:27). Thus, no flame is ever used, allowing for a significant reduction in signal interferences compared to traditional AAS (Pollard and Heron 2008:27; see, however, Van Loon 1985:30-36 for background noise problems with earlier machines).

Another type of AAS useful for the study of trace elements is hydride generation atomic absorption spectrometry (HGAAS). HGAAS involves rendering the analytes in a given sample as inorganic ions through some form of chemical digestion (Yoshinaga *et al.* 1997:5). The sensitivity one achieves with HGAAS is superior even to ETAAS when testing for the presence of lead in a sample (detection limits are 0.6ng/ml and 17ng/ml, respectively). Thresholds this low (in the parts per billion), however, are more useful to medical and environmental investigations, rather than bioarchaeological studies. Such small levels of lead, say, in the bloodstream or a waterway are of critical concern to health and ecology professionals, but given the extended period of exposure represented by lead in archaeological bone, analytical techniques capable of identifying one part per million are perfectly satisfactory (and simpler than HGAAS; Yoshinaga *et al.* 1997:9).

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY

Inductively coupled plasma atomic-emission spectroscopy (ICP-AES, also known as inductively coupled plasma-optical emission spectroscopy, ICP-OES) for the analysis of lead in archaeological bone is not very well documented, though a few researchers have employed the technique to determine its usefulness for other trace element analyses (see Baraybar and de la Rúa 1997; Burton and Price 1999; Zlateva *et al.* 2003). One reason might be that other elements in a bone sample matrix might interfere with the calculation of bone lead (Zlateva *et al.* 2003:204). However, such an obstacle may be overcome in the future, and given its similarity to other techniques below, ICP-AES is included for discussion.

The device itself functions similarly to AAS, except that it measures light emitted by the excited atoms of a given element, rather than the light absorbed by the element. As with absorption, the intensity of emitted light is directly proportional to the element's concentration in a sample. However, it is not merely AAS in emission mode. Atomic absorption spectrometry can be used in 'emission mode,' but there can be a significant loss of analytical sensitivity due to the behavior of elements at different temperatures of the flame. If the flame becomes more energetic, atoms might be excited into a higher energy state and will only

emit their characteristic wavelengths as they return to their lowest energy levels. At even higher energy levels, atoms may ionize and not be detected at all, thus rendering traditional atomic emission spectrometry occasionally problematic (Pollard and Heron 2008:28).

Herein lies the other critical difference between ICP-AES and traditional AAS. Inductively coupled plasma atomic-emission spectroscopy does away with the gas burner in favor of a plasma torch, which can burn at temperatures of 8,000-10,000°C (Pollard and Heron 2008:29). The torch itself is simply a series of three concentric silica tubes with a copper wire wound around the top on the outside. A small volume of argon gas enters through the central tube, while larger volumes are introduced tangentially between the outer two tubes. When it burns, the plasma generated in the central tube is lifted above the torch via the toroidal flow generated by the other gas as it spirals upward between the outer two envelopes of the torch. This lifts the flame away from the burner, which would otherwise instantly melt. Heat is maintained via “a high-power radio frequency alternating current which is passed through the copper coils surrounding the torch, which causes the charged particles in the plasma to flow through the gas in a circular path by induction” (Pollard and Heron 2008:29).

This design requires that the sample be in a liquid form which can then be injected into the fuel argon. The extremely high temperatures of the torch put the atoms into a very excited state, which in turn emit their characteristic lines. These lines are then separated via the diffraction grating and slit used in AAS. A computer-controlled detector (photomultiplier or charge-coupled device) can then determine the emission intensity for a variety of elements sequentially, although the software sophistication used in automated ICP-AES allows analysis to be quasi-simultaneous. For industrial applications, ICP-AES has come to almost completely replace AAS for multi-element analyses, and improvements are constantly being developed. For archaeology, ICP-AES has not received an enormous amount of attention, but due to its greater sensitivity than AAS, the potential remains for a wider application in archaeological investigations (Pollard and Heron 2008:30-31).

As researchers probe more deeply into trace element studies of archaeological bone, the need has arisen to quantify not simply a certain element, but the isotopic ratios of the elemental concentration itself. However, neither AAS nor ICP-AES technologies can provide the kind of isotopic sensitivity required for such investigations. But an instrument which directly borrows from ICP-AES can.

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Inductively coupled plasma mass spectrometry is a mass spectrometry technique which uses ICP as its source for element ionization (most elements are ionized nearly 100%). Other ionization instruments have been used for archaeology, including thermal ionization MS (e.g. Bower *et al.* 2005) or isotope dilution MS (e.g. Carlson 1996), but inductively coupled plasma mass spectrometry has likely received the most attention in trace element studies of archaeological bone (e.g. Reinhard and Ghazi 1992; Djingova *et al.* 2004; De Muynck *et al.* 2008).

The plasma torch itself is of the same design as that described above for ICP-AES, but the detection methods and technologies are very different. As opposed to electromagnetic radiation intensities and wavelengths, ICP-MS creates positive ions which are then detected and quantified by a mass spectrometer (Pollard *et al.* 2007:196). Since its commercial introduction in 1983, ICP-MS has come to replace other elemental quantification technologies (Pollard *et al.* 2007:195-196). "ICP-MS possesses the multi-element analysis capability of ICP-AES and the high sensitivity of ETAAS; in fact, the sensitivity is superior to that of ETAAS for most of the elements" (Yoshinaga *et al.* 1997:18). For lead, ICP-MS is capable of quantifying its concentration in a sample down to a detection limit of 0.8 parts per trillion, a sensitivity threshold which no other technology currently surpasses (Yoshinaga *et al.* 1997:18).

Because the ICP torch is being used specifically to produce ions, a different detector than those mentioned thus far is required for isotopic identification and measurement. In order to accomplish this, a mass spectrometer is required. Mass spectrometry is based on a simple manipulation of electrostatics, namely that the motion of electrically charged atoms can be controlled via external electrical and/or magnetic fields. This means that positively charged particles (ions) can be separated according to their atomic mass-to-charge ratios (m/Z). This allows for the quantification of each type of ion present in the sample, and these direct measurements can be expressed as ionic ratios (Pollard and Heron 2008:56). These ionic ratios give the sample its unique isotopic signature, which in the case of lead in bone, can then be related to exogenous sources in the natural and cultural environments.

In ICP-MS, samples can be tested either as solutions (as will be discussed here) or as solids (using laser ablation, discussed below). The liquid sample, in aqueous or acid-dissolved form, is pumped through a thin tube which feeds directly into the instrument's nebulizer. Argon gas is then mixed with the sample so

that droplets containing the analyte(s) are “expelled from the tip of the nebulizer” (Pollard *et al.* 2007:196). The size of the aerosols in the argon/sample mist is then reduced via condensation so that the sample is introduced evenly. Approximately 1% of the sample is then injected into the plasma torch, leaving the remainder available for additional testing (Pollard *et al.* 2007:196).

Kept under vacuum conditions to keep the positive ions from scattering (and to prevent technological malfunctions), the ICP-MS interface allows the ions produced in the plasma to be “injected directly into a MS” (Pollard and Heron 2008:31). The spectrometer then separates the ions according to their charge and mass, and can count them individually. This allows for the generation of isotope abundance ratios for the element under study (Pollard and Heron 2008:31).

Numerous analyzers exist for mass spectrometry, but that which is used most frequently for biological and environmental studies is the quadrupole analyzer coupled with an ICP ionizer (Shotyk and Le Roux 2005:244; Ewing 1985:395-428). The technological advantage of using a quadrupole analyzer is that it allows for ions to be separated according to their mass-to-charge ratios without having to use a powerful magnet (recall that the ions can only be controlled in an electric and/or magnetic field). A quadrupole is essentially a group of four straight, parallel rods (two on a y axis, two on an x axis) between which the ionized beam passes. Each rod is connected to its diagonal opposite by an electric charge, and the two pairs are “connected to opposite poles of a DC source and also to an RF [radio frequency] oscillator” (Ewing 1985:408). The voltages of these electric currents (DC and RF) can be varied within a “narrow range of frequencies” provided that the ratio of the two sources is kept constant. If the ratio of DC to RF becomes too great (>0.168), ionic trajectories will become unstable and significantly reduce analytical sensitivity (Ewing 1985:410). The ions then pass onto the MS for separation and measurement. When testing for numerous elements, a multiple collector analyzer is used (MC-ICP-MS), but single collectors can be used if only one element is to be quantified.

When the conditions have been optimized for ionization and mass spectrometry, ICP-MS is a very versatile, sensitive instrument capable of detecting numerous elements during the same analysis with a high degree of precision and reproducibility. It is important to consider the research design needs before selecting ICP-MS as the analytical procedure, as the sophisticated instrumentation is fairly expensive and

requires more skill to operate (Pollard and Heron 2008:33). Nevertheless, if destructive analyses are deemed permissible, ICP-MS can be an ideal device to cover a variety of research needs.

But one technological adaptation minimizing sample destruction is worth noting. The ICP-MS can actually be coupled with a laser capable of ablating minute samples from solid archaeological materials. Known as laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), small areas of a solid sample can be evaporated via a high energy, pulsing ultraviolet laser. Housed inside a chamber with argon gas, the evaporated sample is then passed directly from the chamber into the plasma and onto the spectrometer. The area to be sampled depends on the number of elements to be analyzed, but is generally 2mm^2 , making it a minimally destructive sampling technique.

Unfortunately, the technology itself is presently limited. The laser ablation has a far less sensitive detection threshold, may under-represent some samples, and is currently only a surface technique (Pollard *et al.* 2007:198-199). However, LA is mentioned here as a potential candidate for a new, upcoming generation of technologies that may be able to overcome some of the current disadvantages associated with sample preparation. Even in its current state, however, LA-ICP-MS has found some use in creating elemental profiles for bioarchaeological tissues (see Budd *et al.* 1998; Cusina *et al.* 2007; Giussani *et al.* 2009:14-15). As the product undergoes continuous development, LA-ICP-MS may become the mainstay of archaeological chemistry, sensitive enough to compete with other methods while remaining far less invasive.

X-RAY FLUORESCENCE

X-ray fluorescence (XRF) analysis takes advantage of the same principles of atomic electricity outlined above, but instead of utilizing visible light wavelengths, XRF detects the smaller wavelengths in the X-ray field of the electromagnetic spectrum. Simply stated, XRF devices direct a small beam of primary X-rays on a given sample, creating inner shell electron vacancies (K, L, and M shells) which de-excite by fluorescing secondary X-rays. Wavelengths from these secondary, fluorescent X-rays are characteristic of the sample's elements, and upon comparison with known X-ray energy values for a given element (or series of elements), the sample element(s) can be identified and quantified by the XRF detector (Pollard *et al.* 2007:101; Notis *et al.* 2007:206).

When the secondary X-rays return to the detector, other components from the irradiated sample are present as well. These physicochemical artifacts need to be sorted out to remove any spurious findings which could alter the true quantity and type of element present in the sample. The use of a spectrometer can compensate for any results interfering with the chemical data, the most appropriate type of which (for archaeological purposes) is an energy dispersive X-ray fluorescence spectrometer (EDXRF; Pollard *et al.* 2007: 102-103; Pollard and Heron 2008:44-45).

Energy dispersive X-ray fluorescence provides an inexpensive, fast, accessible, and sophisticated means of quantifying elemental surface deposits. This method measures the energies of fluorescent X-rays via a solid state detector which “provides an electronic output that is proportional to the energy spectrum of the X-rays emitted by the unknown sample, simultaneously measuring the energy of the incident photon [the X-ray particle returned to the detector] and counting the number of photons with known energies” (Pollard *et al.* 2007:102-103). Provided that excellent quality control protocols are observed, the EDXRF detector can identify and quantify multiple elements simultaneously. Accompanying software can correct any of the spurious variables that might interfere with the data (see Pollard *et al.* 2007:102) and provide reliable calibrations for each run (Pollard *et al.* 2007:103-104).

However, EDXRF has its drawbacks. For heavier elements such as lead, the energies fluoresced from an irradiated sample might be too great in some cases for the detector to absorb, passing right through it and thereby reducing sensitivity. This methodology cannot reliably detect below 0.1% of a given element and may not be useful to certain project designs. Another disadvantage is that EDXRF machines which use a silicon-lithium crystal detector must be kept at liquid nitrogen temperatures to reduce electronic noise interference and to keep the lithium from drifting (Pollard *et al.* 2007:103). However, this has been ameliorated by the use of high-purity germanium detectors, which can operate at room temperature.

In recent years, XRF devices have become available in compact portable units which can be taken to artifacts for analysis. This advantage is unique in archaeological elemental analysis, and is well suited to a number of research designs. While great progress has been made in terms of the accuracy, resolution, and reliability of handheld, portable XRF devices (PXRF), they are all still limited by one critical factor which makes their application as a nondestructive method to *biological* archaeology rather limited. This same limitation is true of all XRF techniques, portable or not.

Due to their shallow penetration (~20-200 microns, depending on the sample matrix, analyte, and operational voltage), the X-rays are only truly suitable for surface analyses (Notis *et al.* 2007:260). The reason for this is the attenuation of the X-rays as they pass through a given sample. While the primary X-rays may be able to penetrate relatively deeply into the sample, the secondary X-rays can be absorbed by atoms within the sample as they fluoresce through the sample matrix. Secondary X-rays will not generally be returned to the detector from depths below a few hundred microns, and therefore no quantifiable data regarding deeper regions of a sample can be generated (Pollard *et al.* 2007:102).

As discussed in Chapter 1, the distribution of lead in bone is irregular, sometimes pooling toward the periosteal and endosteal surfaces, sometimes pooling toward the center of the bone. A lack of homogeneous tissue distributions means that one cannot extrapolate results obtained via surface quantification, as one might be able to do with other archaeological materials. Furthermore, because diagenetic factors might concentrate post-depositional lead toward the outer surfaces of the tissue, the quantities detected by XRF may represent some postmortem Pb. So while lead certainly falls within the range of elements capable of XRF quantification, its occurrence in skeletal matrices does not make it an ideal candidate for study.

Thus, XRF as a non-destructive technique may not currently be useful for quantitative studies of lead. However, if the samples can be analyzed in cross-section from a core sample or prepared into a fine, homogeneous powder (ashed, as discussed in Somervaille *et al.* 1986 and Wittmers *et al.* 2002:670), X-ray fluorescence is wholly appropriate. Since most lead-in-bone analyses are destructive anyway, using XRF, particularly as a portable instrument, may still offer distinct advantages over more costly, non-transportable techniques.

PROTON-INDUCED X-RAY EMISSION

Proton-induced X-ray emission (PIXE) uses a beam of protons, concentrated on a sample, to produce inner-shell electron vacancies as described above, which then emit characteristic wavelengths as they de-excite. Again, the intensity of emission is measured by an energy-dispersive detector, thereby quantifying a given element concentration within the sample. A principal advantage of this technique is not only that it is nondestructive, but it does not require the sample to be situated within the device (used to

produce the proton beam). External arrangements are possible, although because the X-rays must pass through air on their way to the detector, some will become absorbed by ambient gases (Pollard and Heron 2008:49-50). However, background interferences are comparably low, due to the high speeds involved in proton bombardment, and detection thresholds better than 100ppm are possible (Henderson 2008:993; Pollard and Heron 2008:50). Furthermore, PIXE is capable of mapping elemental microdistributions through a sample's surface by backscattering the analyte's protons, a distinct advantage when defining the locations of elemental concentrations (Henderson 2008:993).

As with the XRF techniques, PIXE is surface sensitive, and can penetrate to between 15 and 50 μ m depending on analyte, sample matrix, and power levels used (Henderson 2008:993). However, it remains possible that future developments will be able to improve the depth of analysis and refine sensitivity even more so. Biological archaeological applications for trace metal analysis are possible with the current technology (e.g. Buoso *et al.* 1992; Vuorinen *et al.* 1990; Reiche *et al.* 1999), but the cost and size of the instrumentation may be prove prohibitive for some projects.

NEUTRON ACTIVATION ANALYSIS

One final source to mention is one that, at present, is not well suited to the study of lead. Known as neutron activation analysis (NAA), the procedure involves irradiating a sample with neutrons from a nuclear reactor, which convert the analytes into (artificially) radioactive elements. As the irradiated elements decay, the intensity of their radioactive emissions can be detected and traced back to the parent elements by careful calculation (Pollard and Heron 2008:50-51).

Neutron activation analysis can be an incredibly sensitive technique for a number of elements (detection limits between 10ppb and 10ppm), but lead is not an ideal candidate analyte. It is unclear as to why, but NAA devices cannot detect the metal, possibly due to chemical interferences or the element's radioactive behavior (Pollard and Heron 2008:55). However, the procedure has been successfully applied in biological archaeology in the production of profiles for a variety of other elements (e.g. Edward *et al.* 1984). It is possible to compensate for some of the analytical interferences associated with lead using a technique referred to as prompt gamma neutron activation analysis (PGNAA), but the effects upon sensitivity are easily eliminated by the use of another analytical procedure (Pollard and Heron 2008:55).

And while NAA competes with ICP-MS for sensitivity, it does have the disadvantages of requiring the use of a nuclear reactor, as well as the disposal of spent nuclear materials (Pollard *et al.* 2007:61). While it is unlikely that the technique can eliminate these significant drawbacks, it is hoped that future instruments will minimize them. Furthermore, the difficulties associated with the detection of lead may eventually be overcome, and future researches may be able to reap the benefits of NAA. Technological modifications of the magnitudes necessary to make NAA more applicable may not be immediately forthcoming, but its successful use in archaeological chemistry bodes well for more sophisticated developments.

SUMMATION

The above discussion does not represent the full suite of analytical instrumentation available for trace element studies, but rather those which have either been featured prominently in the literature or which may lead to major technological breakthroughs in archaeological chemistry. Each one presents a series of distinct advantages and limitations which a given investigator must negotiate in view of a project's analytical needs. The following table provides a summary of each technique's benefits and disadvantages to more concisely depict the methodological *status quo* of lead-in-bone analyses.

Methodology	Advantages	Disadvantages
<i>Atomic Absorption Spectrometry</i>	<ul style="list-style-type: none"> - Inexpensive - Fast - High analytical reproducibility 	<ul style="list-style-type: none"> - Cannot quantify multiple elements simultaneously - Signal interferences from the flame - Sample must be liquefied
<i>Electrothermal Atomic Absorption Spectrometry</i>	<ul style="list-style-type: none"> - Greatly reduced signal interferences over AAS - Improved sensitivity over AAS 	<ul style="list-style-type: none"> - Cannot quantify multiple elements simultaneously - Sample must be liquefied
<i>Hydride Generation Atomic Absorption Spectrometry</i>	<ul style="list-style-type: none"> - Superior sensitivity to AAS or ETAAS 	<ul style="list-style-type: none"> - Cannot quantify multiple elements simultaneously - More complex analytical procedure than AAS or ETAAS
<i>Inductively Coupled Plasma-Atomic Emission Spectroscopy</i>	<ul style="list-style-type: none"> - Improved sensitivity over AAS - Near total atomization of sample - Quasi-simultaneous multiple element quantification 	<ul style="list-style-type: none"> - Cannot accurately quantify lead in most samples at present

Methodology	Advantages	Disadvantages
<i>Inductively Coupled Plasma-Mass Spectrometry</i>	<ul style="list-style-type: none"> - Multiple element analysis capability - Lowest detection limits for lead of any methodology - Isotopic quantification - High analytical reproducibility - Solid samples can be used 	<ul style="list-style-type: none"> - Expensive - Requires considerable training and skill to correctly operate
<i>Laser Ablation Inductively Coupled Plasma-Mass Spectrometry</i>	<ul style="list-style-type: none"> - Minimally destructive - Solid samples can be used 	<ul style="list-style-type: none"> - Detection limits are currently low - At present, it is a surface-sensitive procedure
<i>X-Ray Fluorescence</i>	<ul style="list-style-type: none"> - Nondestructive - Portable - Multiple element quantification 	<ul style="list-style-type: none"> - Surface-sensitive procedure
<i>Energy Dispersive X-Ray Fluorescence</i>	<ul style="list-style-type: none"> - Inexpensive - Fast - Multiple element quantification - Nondestructive 	<ul style="list-style-type: none"> - Not yet ideal for heavy elements - Unsatisfactory detection limits at present
<i>Proton-Induced X-Ray Emission</i>	<ul style="list-style-type: none"> - Nondestructive - External sampling - Can map elemental microdistributions 	<ul style="list-style-type: none"> - Unsatisfactory detection limits at present - Surface-sensitive procedure - Expensive
<i>Neutron Activation Analysis</i>	<ul style="list-style-type: none"> - Satisfactory analytical sensitivity 	<ul style="list-style-type: none"> - Cannot yet detect lead - Must acquire and dispose of nuclear materials - Requires a nuclear reactor

Table 3.1 – A comparison of the methodological advantages and disadvantages discussed in this chapter.

It is clear from the table above that no methodology is without its flaws, and a careful appraisal of each technique's strengths and drawbacks is essential to the development of good data. However, archaeological chemistry is a dynamic field, and methodological imperfections are constantly undergoing improvement. The future of analytical chemistry's role in archaeology will be largely dependent upon the continuous technological refinement of the above methodologies and the development of new ones. Researchers in the decades to come will doubtlessly possess a more sophisticated battery of physicochemical instrumentation, which may resolve some of the current difficulties associated with trace element analyses of human bone. It is likely that sampling procedures will become less invasive, automation systems more precise, and data generation increasingly sensitive and accurate. Hopefully, these operational improvements will expand the field's capacity for interpretation, laying bare new pieces of information otherwise unattainable.

CHAPTER 4

A History of Heavy Metal: The Use of Archaeological Bone-Lead Analyses

During the past 50 years, numerous archaeological investigations have incorporated the analysis of lead in excavated human remains using a sequence of increasingly sophisticated physicochemical instrumentation. While many early investigations were purely descriptive (e.g. Jarcho 1964; Mackie *et al.* 1975; Waldron *et al.* 1976; Blakely and Beck 1982; Rathburn and Scurry 1983; Rathburn 1987), later researchers attempted to correlate lead levels to theorized social practices (e.g. Aufderheide *et al.* 1981, 1985; Handler *et al.* 1986; Ghazi *et al.* 1994), cultural affinity (e.g. Carlson 1996), and migration patterns (e.g. Bower *et al.* 2005). The great strides taken in methodological refinement have enabled researchers to apply chemical data to important archaeological questions, bolstering the powerful utility such analyses have for understanding past peoples.

Lead analyses have been conducted on a variety of sites, including those from prehistoric (e.g. Grandjean *et al.* 1979; Rogers and Waldron 1985; Gonzales-Reimers 1999), ancient (Mackie *et al.* 1975; Waldron 1976; Ericson *et al.* 1979), and medieval contexts (e.g. Barry and Connolly 1981; Carvalho *et al.* 2004) to the modern historic era (see below). However, due to this paper's focus on historic archaeology (post-contact North America/Caribbean), the following historiography will draw primarily on the seminal studies from this subdiscipline. In some cases, literature from other contexts has been included for review due to analytical novelty or overall originality.

This chapter will critically examine several studies in detail, underscoring the merits and limitations of each. In part, this has been undertaken to provide perspective on the field's progression, but is also useful to emphasize how chemical analyses can contribute otherwise unavailable evidence to archaeological investigation. In some cases, lead data has possibly misled researchers, whereas in others it has served to more fully develop archaeological conclusions.

LEAD AND SOCIAL BEHAVIOR

It is instructive to begin with a study that moved beyond the tradition of merely descriptive bone-lead analyses. Aufderheide *et al.*'s 1981 study of lead in Chesapeake planters and laborers at Clift's Plantation (early 18th century), Virginia is one of the earliest examples of correlating lead intake with

socioeconomic status. Attempting to draft archaeological inferences about social behaviors based on toxic trace elements is an intriguing pursuit, but must be executed with meticulous care.

The 1981 study examined 16 burials of both Europeans and Africans, spatially segregated in the burial grounds according to historically specific social practice (Aufderheide *et al.* 1981:287-288). The physical separation of interments according to jurial status (i.e. free whites vs. enslaved Africans) likely reflects social controls which informed historical attitudes, a fact which can be substantiated by archaeological analysis. The authors were principally interested in determining if skeletal lead burdens significantly differed between the two cemetery groups. The logic here is that the planter class, having access to numerous lead artifacts (pewter wares and lead-glazed ceramics), should have considerably higher lead burdens than the laborer class, for whom access to these materials was strictly limited. With the separation of planter-laborer living quarters toward the close of the 17th century, it is likely that laborers would no longer share the same food and drink vessels (Aufderheide *et al.* 1981:287). Thus, the planter class would have continued exposure to lead-contaminated foodstuffs while the laborers after this time would not.

Lead concentrations were determined via ETAAS from different skeletal core samples for each burial. Individual lead burdens were found to be between 128 and 258ppm for the planter group, while a range of 8-96ppm characterizes the laborer group (Aufderheide *et al.* 1981:289-290). All lead burdens correlate with age (young children excepted; see Chapter 1), and the spatial distributions seem to support the hypothesis at first. However, there are some problems with this data that remain unresolved.

This early study of skeletal lead burden does not take into account the possibility of diagenetic alteration. Soil chemistry was not analyzed to determine elemental and isotopic quantities of lead near or in the burials and any conclusions must be considered tentative. Assumptions about Pb in the soil-skeleton interface must be empirically tested. Even if the actual lifetime lead burdens of these individuals correlate well with physical location in the graveyard, a diagenetic assessment could determine if the levels revealed archaeologically have been altered via soil uptake. For this sort of study, it would be necessary to calculate concentrations of lead isotopes in the soils and the bones via ICP-MS, although this technique was not readily available when the study was conducted.

Assuming for a moment that the values obtained actually reflect lifetime lead exposures, one must implement other lines of evidence for reconstructing social variables. In this paper, the historical and archaeological documentation complements the analytical findings well, but to have an archaeological site so well characterized in the historical literature is rare. It seems appropriate, then, for the researchers to have attributed higher lead concentrations to differential access to lead material culture, but a consideration of other processes at work is necessary for robust archaeological interpretation. Lead burdens do not comprise the sole line of evidence in this study. However, when one comes across spatially distinct differentiations in skeletal lead concentrations, differences in local burial environments must be taken into account. Furthermore, other factors which might contribute to the inordinately high levels of lead in the planter family must be scrutinized (e.g. it could be occupational, rather than domestic in origin). Nevertheless, this study provides a good example of the kind of interpretive power lead analyses can have for an archaeological site.

Aufderheide *et al.* returned to the notion of correlating lead with social practice in 1985. Four sites were selected for study, each comprising a different demographic constituency: 24 enslaved Africans at Catocin Furnace, MD; 17 possibly free individuals, most of mixed ancestry at College Landing, VA; numerous individuals from mixed temporal contexts from Governor's Land, VA; and 16 whites from Irene Mound, GA. Lead concentrations were assessed for all individuals using ETAAS, and burial soils were tested for lead to determine the possible extent of soil-bone exchange via an unstated method.

The results were similar to those obtained in 1981: lead concentrations were typically higher in the planter class whites than those in the servant/laborer category. The mixed ancestry at College Landing accompanies a wide range of lead burdens for this group, which the authors interpret as demonstrating various degrees of economic success. The other two sites showed a range of lead values, all sufficiently high to lead the authors to believe that leaden domestic wares were responsible for intoxication (Aufderheide *et al.* 1985:354-360).

As with the 1981 study, it is assumed that the primary source of bioavailable lead comes from domestic wares used in the storage, preparation, and consumption of food and drink. This alone is somewhat problematic, not only because it excludes other pathways of intoxication, but the assumption is based on historical trends in planter materiality rather than the recovery of cultural material in most cases.

To be fair, the planter class generally shows similar values between men and women, which the authors conclude must be caused by a shared domestic source. However, while the historical documentation and archaeology of the colonial period speak of pewter wares and lead-glazed ceramics as significant lead reservoirs, one cannot assume that correlation equals causation.

Furthermore, as with the 1981 study, a detailed description of the analytical procedure employed is not given, thereby leaving questions concerning the handling, storage, and treatment of the skeletal materials (there is a possibility of post-excavation contamination). In terms of postdepositional contamination, the authors did employ soil chemistry procedures and found relatively high levels of lead in soils adhering to skeletal elements, but discounted their contribution to the overall burden (even in acidic soils) for reasons not readily apparent.

Lead in acidic soils is certainly available for diagenetic uptake, but why the soil ions are not given due consideration is strange. Isotopic analysis via ICP-MS of both soil and bone samples could reveal correlating ratios indicative of postmortem acquisition (or the opposite, or an admixture). This is particularly important in the case of Irene Mound which revealed a very wide range (4.9-183.8ppm) for presumably white individuals, but no soil was recovered from this site for testing (Aufderheide *et al.* 1985:360). Since the authors rely on foodways to explain lead burden variations, this sample would almost have to be discounted since no documentary or archaeological evidence suggests the social status of each individual.

Though the aim of the study is intriguing, the conclusions are problematic and may be based on erroneous data. In the case of the Irene Mound group, it is lead content alone that is assumed to index social, even marital status, but clearly additional evidence is necessary. The correlation of lead burden to wealth (Aufderheide *et al.* 1985:380) is simplistic and deprives the conclusions of deeper meaning. This is a clear example of the reach of archaeological interpretation overextending its grasp, but it is still a novel, comparative study which can be lauded for its objectives and the technology it employs.

LEAD, SOCIAL BEHAVIOR, AND PATHOLOGICAL TRENDS

Similar to the reports by Aufderheide *et al.*, Handler *et al.* (1986) and Corruccini *et al.* (1987) use archaeological skeletal lead to help understand past social processes, but from a different context. These

studies are the only historical archaeological reports on skeletal lead burdens from the Caribbean, and are derived from a cemetery of enslaved Afro-Barbadians at Newton Plantation, Barbados. Excavation work was conducted in the 1970s, during which time 104 individuals were recovered, of whom 48 were tested for lead (Corruccini *et al.* 1987:234; Handler *et al.*, 1986:401-402). Due to differential preservation, various skeletal elements from different individuals were sampled, though all of the samples were cortical bone cores that were cleaned and submitted to ETAAS for quantification (Corruccini *et al.* 1987:234).

A range of values from 0 to 424ppm lead were obtained, and patterns in skeletal intoxication were developed using standard statistical protocol appropriate for the study (Corruccini *et al.* 1987:234-236). In general, the following trends were observed: females had a wider range of lead levels than males; individuals of presumed African birth (based on tooth mutilation) had significantly lower levels than those deemed Barbadian-born; and the minority of burials oriented to the north (possibly suggesting African birth) had lower lead toxicities than the majority (Handler *et al.* 1986:402-403; Corruccini *et al.* 1987:236-237).

The authors relied on historical documentation to devise possible lead reservoirs, and concluded that Newton's enslaved had far greater access to leaden materials than their mainland colonial counterparts. Historical literature suggests that some of the diagnostic symptoms of lead poisoning were exhibited widely by both free and enslaved Barbadians during the period under study (1660-1820). None of these sources speaks directly to Newton Plantation, but it is assumed that these generalized pathologies could reasonably be exhibited by the enslaved at Newton (Handler *et al.* 1986:408-410).

The most likely source of exposure was determined to be the consumption of rum produced with distillation machinery built, in part, of lead (Handler *et al.* 1986:412-417). Historical evidence suggested that rum would have been available to the enslaved for consumption, and that rum production itself likely leached considerable quantities of lead into the spirit from the processing equipment. Therefore, the authors conclude, rum is the most likely culprit for at least some of the lead levels observed in the Newton skeletons (Handler *et al.* 1986:417-418; Corruccini *et al.* 1987:238).

Lead concentrations were used to provide chemical evidence for historically documented Barbadian lead poisoning epidemics. However, these studies are mentioned here as a cautionary tale. Firstly, no information is given regarding soil chemistry, and diagenetic uptake is dismissed outright. This

is difficult to bypass, given that most plantations had their own distilleries (Handler *et al.* 1986:415), enhancing the potential for local environmental contamination. As with most studies, isotopic analysis of soil and bones could reveal ratios suggestive of ionic exchange within the burial environment.

Secondly, there is a problem with the conclusions which they draw, diagenesis aside. While rum could contribute to the Newton lead burdens via consumption, it is also possible that slaves involved in processing the spirit (or the processing of sugar itself) became exposed to contaminants due to continuous contact with the lead machinery. Rum distillation would seem to offer a variety of opportunities for exposure, only one of which is ingestion of the final product. To be fair, historical literature suggests that the enslaved on Barbados frequently drank rum, but extrapolating this to Newton is speculative. And while the authors admit that other pathways of intoxication are possible, they adamantly rely upon rum drinking as the primary vector.

Lastly, it is the principle goal of these studies to provide physical evidence for a diachronic lead poisoning epidemic in the West Indies, but this is not well substantiated by the analysis. Not only are the data extrapolated beyond appropriate geographical and historically-particular boundaries, but the estimation of blood lead levels (which would correlate to symptomology) from bone lead levels is admittedly problematic (Corruccini *et al.* 1987:238). The equations used by the researchers to derive blood lead levels from bone lead burdens are imprecise, and so it is difficult to correlate skeletal toxicities to certain symptoms without over- or underestimating the physical effects of intoxication.

As noted, these examples are included not only because of the singularity of their sample population, but because they strive to accomplish more than can be reasonably expected. Studies from the Newton group are admirably ambitious, but need to be tempered by an acknowledgement of the inherent limitations associated with the methodologies and interpretive frameworks used.

NUTRITION AND A NOVEL METHODOLOGY

Considering alternate methodologies is important for archaeological inquiry, and a knowledge of what has been accomplished via different analyses is helpful. Though it falls outside the purview of historical archaeology, Vuorinen *et al.*'s 1990 study of trace metals in Roman infant bones is useful to briefly mention for its diagenetic considerations and PIXE analysis. Long bones from 19 Roman infants

(fetus to 1.5 years old) were analyzed for a variety of elements, among them lead, in order to develop a notion of past nutritional and dietary conditions. After proper cleaning protocols were observed (Vuorinen *et al.* 1990:238-239), cortical samples were submitted to PIXE for lead quantification, which returned values of 34.3ppm on average (Vuorinen *et al.* 1990:249). The authors were cautious, however, in attributing these levels to lifetime exposures due to the poor state of preservation and the diagenetically-vulnerable thin skeletal tissues characteristic of child remains.

Soil samples were collected two years after the bones were excavated, and are therefore not directly derived from the burial environment. Data from soil analysis cannot be strongly correlated to bone values, but can provide some perspective on the possibility of soil-bone exchanges (Vuorinen *et al.* 1990:245-246). Several samples at various depths were collected to provide a general site profile, and analyzed for lead using AAS. Even with such a sensitive technique, the authors are keenly aware that more sensitive and sophisticated soil analyses would be ideal (Vuorinen *et al.* 1990:251).

Lead values were determined to be likely diagenetic in origin, given the poor state of preservation and the high correlation with iron (which may facilitate lead's mobility – see Chapter 2). Even though the samples were analyzed with PIXE, the potential for diagenetic change limits the capacity for archaeological inferences. Thus the strength of this paper lies in its use of a minimally destructive technique, as well as its reluctance to draw conclusions regarding cultural behavior based on lead levels which may be compromised.

TRADE PATTERNS AND FUNERARY PRACTICE

An alternate methodological approach was utilized by Reinhard and Ghazi (1992) and Ghazi *et al.* (1994) for characterizing lead in a different demographic altogether. Their work is an early example of utilizing ICP-MS in historic archaeology, attempting to measure elemental and isotopic quantities from a series of 39 Omaha Native Americans (Nebraska) from the period 1780-1820. Six of these individuals displayed very high concentrations and were selected for isotopic analysis to determine the origin of the lead (Reinhard and Ghazi 1992:185).

Rib fragments (trabecular tissues removed) from these individuals were sampled and prepared according to standard protocol, and submitted to ICP-MS for both elemental and isotopic quantifications.

Standard reference samples were incorporated for calibration purposes. A variety of soil samples characterizing undisturbed soil, soils from burials with lead artifacts, and soils from burials without lead artifacts were collected and analyzed to determine soil lead concentrations in different contexts (Reinhard and Ghazi 1992:185). Lead artifacts associated with burials were also analyzed for total lead content.

The results presented by the team are interesting. The soil samples yielded average concentrations around 16.5ppm, while the artifact analyses found that only 8% of burial goods were pure lead (Reinhard and Ghazi 1992:186). However, the values for the human samples are most striking, returning results of between 4.8 and 2,567ppm (Reinhard and Ghazi 1992:186-187).

Most of the bone values are considerably higher than those found for the surrounding soils, and therefore diagenetic uptake of lead, while a possible contributor to overall lead burden, is deemed an unlikely source for most of the skeletal lead (Reinhard and Ghazi 1992:188). Nor is it likely that leaden burial artifacts contributed much in the way of postmortem lead to the Omaha remains, simply because materials of this sort were only associated with a few of the interments (Reinhard and Ghazi 1992:189). Therefore, the authors examined isotopic ratios from six individuals compared with artifact and local lead deposit ratios. While the ratios between skeletal lead, artifact, and deposit did not align perfectly, the authors suspect that the utilization of lead artifacts from a variety of origination points (deposits) contributed to the skeletal make-up (as there was some agreement between artifact and deposit ratios; Reinhard and Ghazi 1992:190-191).

Metabolic lead alone cannot explain some of these values (many exceed clinical observations), and so the authors suggest that cultural practices such as painting the dead may have contributed to the strangely high concentrations observed (Reinhard and Ghazi 1992:191). Differences in male and female lead levels suggested that perhaps males were more involved in the manufacture and ingestion of lead than females. Subadults exhibited the greatest variation and highest concentrations of lead, suggesting to the authors that trade with Euroamericans for lead materials put children at a greater risk of lead poisoning (coupled with their natural physiological susceptibility – see Chapter 1; Reinhard and Ghazi 1992:192-193).

While the authors attribute lead intoxications to patterns of local trade or manufacture, their conclusions remain admittedly tentative (Reinhard and Ghazi 1992:194). They were unsuccessful in

distinguishing metabolic lead from postmortem contamination, and seemed reluctant to consider the possibility that local soils could have contributed significant amounts of lead to the bone. In order to more fully develop this, the authors should have quantified lead isotope ratios from the soil for comparison with the other materials in this study.

But the success of this study remains clear nonetheless. The use of ICP-MS represents a comparably sophisticated methodological application in pursuit of skeletal lead's cultural etiology. Unsatisfied with ambiguous results, Ghazi *et al.* (1994) returned to these samples and identified that many had received postmortem applications of lead-containing paints, which resulted in unusually high skeletal burdens. Lead values for those who did not receive funerary painting were attributed to metabolic intake. Higher values for children are consistent with higher absorption rates, while adult values are more moderate and likely reflect lifetime acquisition (Ghazi *et al.* 1994:431). But by examining lead burdens in the context of body paints, the authors were able to provide chemical evidence for historic trade practices as they existed along the Missouri River.

The phenomenon of past trade patterns provides a useful context in which to test archaeological theories using bone-lead analyses. Trade practices themselves bring various peoples and materials into contact with one another, and many of these variations are biologically represented. Using skeletal lead to identify individuals of different cultural backgrounds brought together by trade is a fascinating pursuit, and one which has been carried out quite successfully.

ISOTOPES AND CULTURAL AFFILIATION

In 1996, Carlson published a study which sought to differentiate individuals of varying cultural affiliations from a 19th-century Albertan fur trading post based on differences in skeletal lead isotope ratios. Earlier researchers used gross elemental concentrations to address issues of social status in cemeteries containing individuals of differential socioeconomic standings, but isotopic data provide a refined, more revealing approach. Using lead isotopes for the purpose of identifying cultural affinity was not unheard of in historical archaeology prior to this (e.g. Kowal *et al.* 1991), but the nature of Carlson's sample truly put the efficacy of such a methodology to the test.

Samples in this study include eight individuals from the Hudson Bay Company's Rocky Mountain House fur trading post, in operation between 1835 and 1861 (Carlson 1996:558). Skeletal morphologies were used to estimate ancestry, resulting in the identification of two Native Americans, one Caucasian, and five persons possibly representing a mixed ancestral affiliation. The eight samples were divided into two sociocultural groups: one representing the two Native Americans, and the other representing six individuals suspected to have lived and worked at the trading post.

In order to address cultural affinity based on isotopic signatures, cortical skeletal samples were submitted to mass spectrometry from each individual. Potential diagenetic interferences were assessed and found to be minimal based on an alkaline soil profile, the relatively brief periods of interment (ca. 135 years), the over good condition of the bones, the removal of periosteal and endosteal tissue surfaces, the very low concentration of readily exchangeable (i.e. soluble) lead ions in the soil (0.012ppm), and the great differences between tissue and soil isotope signatures. Thus, while diagenetic influences are impossible to rule out, it seems highly unlikely that diagenesis plays a major role (Carlson 1996:561-563). Such a careful characterization of the possibilities of post-depositional lead uptake is critical for studies of this kind, and Carlson's scrutiny should be emulated.

Lead-containing artifacts from the site were also tested for isotope ratios, and it was found that most of the skeletal tissues comprising individuals assumed to have worked/lived at the fort align fairly well with the material culture ratios. Isotope signatures from an individual of Native American ancestry aligns much more closely with those from a series of local faunal samples recovered archaeologically and submitted to the same chemical tests. An individual who does not have much access to anthropogenic lead will much more closely align to the lead levels of their natural environment (a good approximation of which would be lead from contemporary local animal bones; Carlson 1996:563-564).

Two samples did not align closely with either group, however, but are instead intermediary between artifact and animal bone ratios. One of these individuals is suggested to have been at the trading post only occasionally, and might therefore be of a different sociocultural background with different lead exposures. The other is a Native American who has exceedingly high levels of skeletal lead. This person could not have acquired such high levels through the natural environment, and certain cultural practices such as chewing lead shot may have contributed to the overall burden (Carlson 1996:564-565).

Carlson is cautious about drawing specific conclusions, recognizing that identifying the sources of ingested lead for any sample is an exercise in educated speculation (Carlson 1996:565). However, it is interesting that certain samples aligned very closely to anthropogenic lead, while others either aligned with faunal data or were intermediate between both. This alone cannot provide an assessment of cultural affiliations, and as Carlson writes, “without historical/archaeological context...the lead isotope data would be primarily descriptive” (Carlson 1996:565). But taken in concert with other evidence, isotope data can be a powerful tool for pursuing archaeological interests.

ISOTOPES AND MIGRATION PATTERNS

Isotopic signatures have gained considerable importance in archaeological bone analyses, and are often much more descriptive than gross elemental concentrations. In 2005, Bower *et al.* assessed both for a population of fifteen individuals recovered from a late 19th-century Coloradan mental asylum. This study has been included for the robustness of its research design and its intriguing analytical ambitions.

Tissues sampled for isotopic analysis included dentine, cortical bone, and bone callus from healing fractures. These three sample types sequester different lead isotopic signatures at different points in life, making it possible to compile “Pb exposure histories...ranging from childhood to shortly before death” (Bower *et al.* 2005:361). Since tooth tissues can capture isotopes from early stages of life, isotopic signatures derived from these tissues can be related to an individual’s broad geographic origins. Cortical bone tissues represent the acquisition of isotopic ratios during life, and knitting bone reveals isotopic ratios close to the time of death. Constructing migration trajectories for individuals thereby becomes plausible when the isotopic ratios from these tissues are compared.

Samples used in this study were analyzed via ICP-OES and thermal ionization MS to retrieve lead ratios for both tissue and soil samples (Bower *et al.* 2005:362). Bone crystallinity was found to be good, indicating that histological diagenesis was fairly limited. As for the acquisition of diagenetic lead, several measures were taken to characterize any possible uptake, which is one of the primary reasons for this study’s review.

Bower *et al.*’s study provides for excellent diagenetic controls. Isotopic analyses of soils and tissues showed that the bones did not align directly with the soils. This was underscored by the ratios from

individuals for whom multiple tissues were sampled; the soil samples lay outside of the trends which tie these samples together, indicating that uptake from the soil is unlikely. Furthermore, no lead artifacts were associated with any graves, and the alkaline nature of the soils, together with the burial depths, severely limit lead's mobility. Lastly, mobile lead from tissues was extracted using acetic acid and other reagents, and the extremely low quantities observed in the extraction indicate that post-mortem uptake is probably negligible at best (Bower *et al.* 2005:366). The attention to diagenesis is robust and reliable, and should be a lesson to any future researcher.

The use of lead isotopes to develop migration trajectories for different individuals is noteworthy. In the three individuals from whom multiple tissue samples were taken (enamel, bone, and knitting bone), plotting the variances in isotopic profiles provides a good sense of their geographic locales at different stages in life. This assumes that the isotopic signatures are derived from acute environmental contamination associated with contemporaneously exploited geogenic sources. It is impossible to state that these are the sources of lead for most cases, as the isotopic ratios between tissue and geologic deposits do not always align perfectly. But lead's limited cultural availability given the spatial and temporal contexts might suggest the metabolic intake of Pb from areas heavily polluted with the metal by manufacturing processes. Migration trajectories for these individuals, then, are plausible, but they cannot be asserted with total assurance.

Creating neat lines of individual migration based on when certain isotopic signatures were biologically sequestered (according to tissue type) is a fascinating potentiality. However, lead alone cannot depict migration, and other lines of evidence, either documentary or chemical (i.e. the analysis of other trace elements, strontium for example) would need to be considered. It also seems extraordinarily difficult to distinguish the ratios of geogenic deposits from lead introduced from other sources, unless the tissue and deposit signatures align extremely well. Nevertheless, this study is an excellent example of how to check for diagenetic alteration, and the research goals are both ambitious and original.

AN ANALYTICAL CAUTION: DIAGENESIS

It is useful to mention one final study in historic archaeology for the applicability of lead analyses to skeletal populations. Wittmers *et al.*'s 2008 evaluation of early 19th-century skeletal remains from

Philadelphia's First African Baptist Church (FABC) reveals that sometimes, even with highly sophisticated technology, factors beyond the control of any research design will severely limit the usefulness of the data generated.

For this study, 135 individuals exhumed from the FABC were selected for lead sampling via ETAAS and XRF microscopy. ETAAS was used to determine overall lead burdens for a variety of cortical bone elements, while XRF was used to map the microdistributions of lead in histological structures with extremely high resolution (down to 1ppm lead with a spatial resolution of better than 10 μ m; Wittmers *et al.* 2008:380).

The researchers found that infants and subadults have lead burdens grossly beyond what would be expected in a living population. Lead burden is a function of age (see Chapter 1), but the soaring values for the FABC led the investigators to conclude that diagenesis was a major contributing factor (Wittmers *et al.* 2008:382-383). The greater porosity of immature bones exposes them to the effects of diagenesis more readily than adult bone, and the pollutant conditions in an urban graveyard would likely exacerbate this.

Variables enabling diagenetic alteration were examined using soil chemistry, histological architecture and integrity, and burial locations. The authors found little relation between soil lead and bone lead concentrations for the FABC group, but the mildly acidic burial soils could have enabled post-depositional uptake. A negative correlation was found between the bone integrity and lead concentrations (as integrity decreased, lead levels increased), and while it was not statistically significant, the authors consider the state of preservation as contributing to diagenetic uptake (Wittmers *et al.* 2008:383-384).

Data generated from XRF mapping indicated that while in some samples lead was concentrated toward bone surfaces, other individuals yielded much more irregular microdistribution patterns. Since separating the suspected diagenetic lead from metabolically-acquired lead is extremely difficult (and inexact at best), Wittmers *et al.* conclude that it is simply unrealistic to assume that the pattern of lead's distribution in bone "can be predictive of bone lead diagenesis" (2008:385).

Thus, this study is included here for review not because of the sociocultural commentary it can offer, but because of its contributions to the diagenesis dialogue (and for its novel use of XRF microscopy). Sometimes it is necessary to forego discussions of lead's ability to reference sociocultural processes for a given time because diagenetic interference poses too great a risk. However, research like this proves that

diagenesis does not leave archaeological inquiry at a dead end, because by further exploring its parameters in cemetery populations, investigators gain a better understanding of how to control for its influences. Without work such as this, the archaeology of lead in bone would not be able to progress as a sensitive, versatile, and unique field of inquiry.

CHAPTER 5

Suggestions for a Case Study: College Landing, VA

This chapter presents a case study that illustrates how the analysis of lead in archaeological bone could be ideally implemented. The case study itself will embody the sophistication of modern analytical instrumentation, and demonstrate how a properly framed lead analysis program can contribute unique lines of evidence to archaeological problems. Given the trials and triumphs of the studies discussed in the previous chapter, the potential pitfalls and rewards inherent in this sort of project should be readily apparent. This chapter will show how a careful research design can navigate the hazards of archaeological chemistry and optimize its significance for constructing meaningful archaeological inferences.

The case study presented below represents how a study of archaeological lead ought to be executed, rather than a program which will actually be undertaken. Instead, the suggestions below comprise a research plan that could have been conducted under ideal conditions. Some of the recommended tests could still feasibly be performed (such as those prescribed for skeletal material), while others simply cannot (such as those prescribed for soil samples). But the following proposal could be applied to any archaeological population for which the materials needed for analysis are available. It may therefore serve well as a general template for future research designs.

HYPOTHESIS 1

If the early 17th-century Tidewater Virginia colonial cemetery at College Landing contains some individuals who were born abroad as well as some who were born in Virginia (as suggested by stable carbon isotope tests), then an analysis of lead isotope ratios will differentiate between those born in the Old World and those born in the New World.

HYPOTHESIS 2

If normal bone metabolism has altered the original lead isotope signatures for some of the remains at CL7, then lead isotope analyses will differentiate between those individuals who spent most of their time in the colonies and those who spent most of their time abroad.

HYPOTHESIS 3

If diagenesis has significantly altered the isotopic composition of the 17th-century College Landing cemetery remains, then lead isotope ratio analyses will not produce a clustering effect based on differential geographic origins, but instead a random scattering of lead signatures altered by the burial environment.

BACKGROUND

During 1986 and 1987, Colonial Williamsburg archaeologists, under the direction of Marley Brown III, excavated an early 17th-century site in the area of Williamsburg, VA called College Landing. Situated about a mile to the south of the city center, this region served as one of colonial Williamsburg's major ports during the 18th and 19th centuries, connecting the burgeoning town to the major trade routes along the James River via College Creek. Portions of the 18th-century port were excavated during the 1986/1987 sessions to make way for a residential development, during which time a much earlier historic site, called CL7, was accidentally discovered (Edwards 1987:v).

While stripping topsoil and plowzone for the construction of a roadbed, numerous archaeological features dating to the first half of the 17th century were revealed. Among these were several graves, post holes, a trash pit, a boundary ditch, and a potential house cellar (Edwards 1987:v). These findings represent one of the earliest historical contexts ever addressed by Colonial Williamsburg's Office of Archaeological Excavation, providing a unique window into an otherwise poorly characterized time of the area's early post-contact period.

Prior to the establishment of Williamsburg in 1699, the area which would become College Landing was part of what was known as Middle Plantation. The Virginia House of Burgesses, operating out of nearby Jamestown, officially passed the "Act for Seating of the Middle Plantation" in 1632. Situated on high ground between the James (to the south) and York (to the north) Rivers, Middle Plantation was established in part to provide some measure against attacks from the peninsula's native peoples. A palisade, stretching between the rivers, was constructed at Middle Plantation to keep Native Americans out and livestock in (Edwards 1987:1). Portions of this palisade have been archaeologically discovered to the north of the town, although its southern extensions remain largely unknown. No documentary or archaeological evidence speaks to site CL7's proximity to the palisade, but given its early period of habitation, the site was

likely located near to the fence line (Edwards 1987:1). However, it is possible that people already lived at CL7 by the time the palisade was built, though this cannot be confirmed (Edwards 1987:15).

From the materials recovered during excavation, CL7 can be generally described as an early domestic site. Most artifacts were categorized as architectural (nails, daub, brick, hinges, &c.), domestic (predominantly animal bone, but also ceramics, utensils, &c.), and personal (tobacco pipe fragments, gun flints, remnants of clothing, &c.). These materials, taken together with a total lack of any military paraphernalia, most likely point to CL7 as a farm rather than a defensive post (Edwards 1987:19).

A series of graves were also located at CL7. Ten individual burials were identified, although most of the skeletal remains were discovered in an extremely poor state of preservation (Edwards 1987:7). No whole bones were found in any of the graves, and in one case (that of a child), only the crowns of the teeth were recovered. Diagenesis had clearly reduced most of the skeletons to mere fragments, all of which were nonetheless properly excavated and stabilized.

The graves themselves contained very few artifacts, other than numerous nails associated with five of the burials. A redware fragment and piece of a Bellarmine stoneware jug were the only other cultural materials discovered within the graves. Neither of these two artifacts is diagnostic of a tight temporal context, but both date the graves to somewhere in the first half of the 17th century (Edwards 1987:7).

MATERIALS AND METHODS

Of the ten individuals that were found, osteological data is only available for eight of them. The rough demographic profiles compiled for each are displayed in Table 6.1. Most variables are difficult to assess given the incompleteness of the recovered skeletal remains. All individuals are assumed to be of European (British) descent.

Grave	Sex	Age (yrs)
CL7-0030	M	25-35
CL7-0014	-	15 +/- 3yrs
CL7-0062	-	17-25
CL7-0063	-	25-35
CL7-0065	-	15-21
CL7-0006	-	1.5 +/- 0.5
CL7-0067	-	<17
CL7-0061	-	25-35

Table 6.1 – Demographic attributes of CL7 individuals

A stable carbon isotopic study was conducted by Harold Krueger at ISOSPEC on behalf of the Colonial Williamsburg Foundation for six of the ten total individuals (Krueger, n.d.). The goal here was to determine the dietary reliance upon different types of vegetable matter, which will vary geographically. In simple terms, the logic is as follows.

Only two stable isotopes for carbon exist, ^{12}C and ^{13}C , of which the latter is more descriptive for characterizing certain plants. Because CO_2 is “the carbon source for all terrestrial plants,” different groups of plants will discriminate against carbon isotopes differently, according to variations in their respective photosynthetic pathways (Larsen 2004:271). Figure 6.1 shows this process.

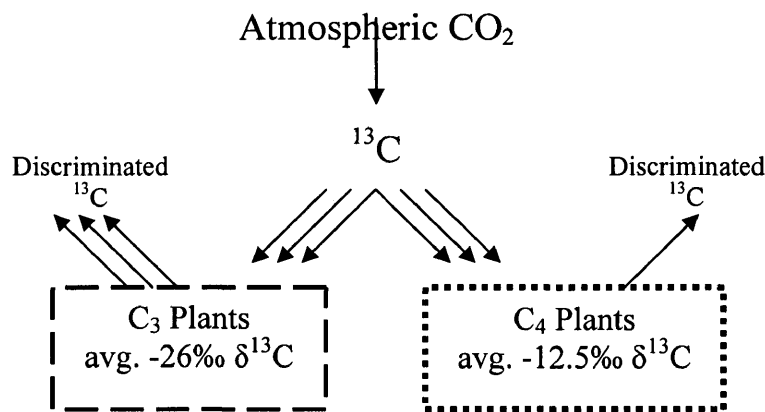


Figure 6.1 – Differential discrimination of ^{13}C by C_3 and C_4 plants relative to reference value δ .

Plants categorized as C_4 (referring to the photosynthetic pathway) do not discriminate against ^{13}C to the same extent as C_3 plants will. Differences between the two are expressed as parts per mil against an international standard, whose value is set at δ . Because C_4 plants discriminate less against ^{13}C , they generally have a less negative $\delta^{13}\text{C}$ value than C_3 plants. Values for each fall in the range of -9‰ to -21‰ for C_4 plants (avg. -12.5‰) and -22‰ to -38‰ for C_3 plants (avg. -26‰; Larsen 2004:271).

Whether a plant has a C_3 or C_4 photosynthetic pathway depends upon the climate to which it has adapted. Plants characterized as C_3 (certain grasses or tubers, for example) generally grow in temperate regions. Those which are categorized as C_4 plants (some amaranths, maize, chenopods, &c.) are more accustomed to hot and dry climates (Larsen 2004:271).

The importance of this to biological archaeology is that humans who consume these different kinds of plants retain the $\delta^{13}\text{C}$ differences, although metabolic fractionation can alter values by roughly 5‰

(Larsen 2004:271). By developing stable carbon isotope profiles for the individuals buried at CL7, a rough estimate of New World versus Old World origins can be formed. Those individuals with a less negative $\delta^{13}\text{C}$ value may have a higher probability of having been born in the colonies (or at least spent most of their time in the colonies), while those with more negative $\delta^{13}\text{C}$ values could have been born in the British Isles (or, again, at least spent most of their time there). This by no means firmly indicates geographic origin, but it provides a useful starting point for attempts to discriminate the different origins for the College Landing remains.

What is interesting is that two distinct clusters were found when stable carbon isotope values were assessed (figure 6.2).

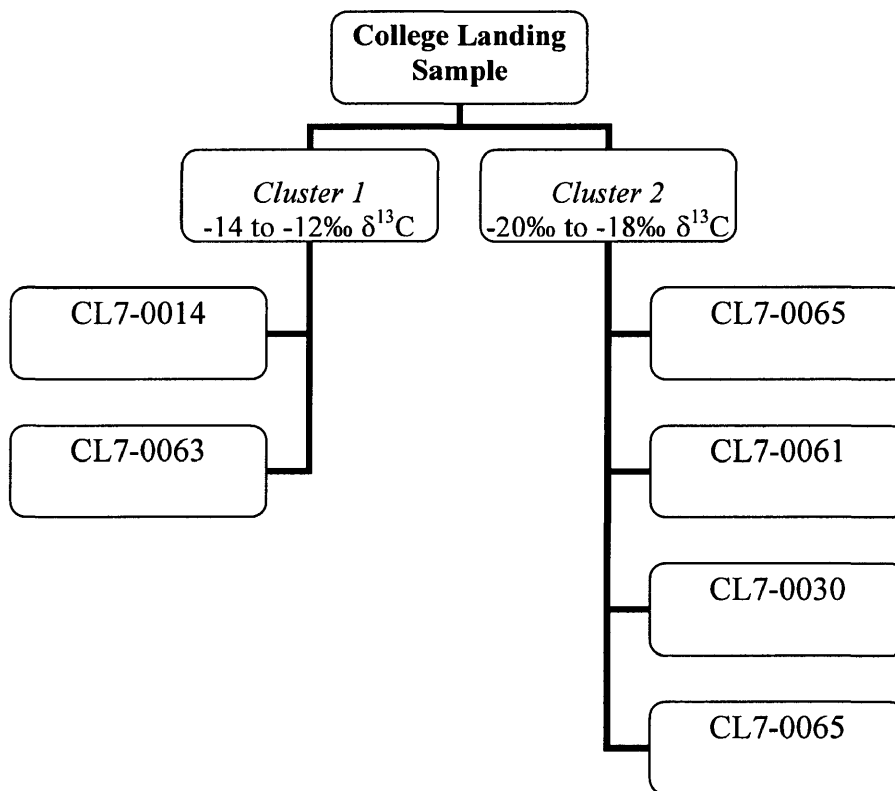


Figure 6.2 – Stable carbon isotope clusters at CL7.

One cluster, consisting of CL7-0014 and CL7-0063, had $\delta^{13}\text{C}$ values very close together in the -14‰ to -12‰ range. The remaining cluster consisted of individuals CL7-0065, CL7-0061, CL7-0030, and CL7-0065, whose $\delta^{13}\text{C}$ values fell into the -20‰ to -18‰ range.

The stable carbon isotope analysis has been dealt with at some length because it is a single line of evidence in need of supplementation via other analyses. Here, then, is the reason for conducting a lead isotope analysis on every available individual from site CL7.

As has been shown in examples from Chapter 4 (e.g. Carlson 1996; Bower 2005), lead isotopes housed in archaeological bone can speak to population origins and migrations. If all of the individuals eligible for analysis have their lead isotopes tested, the results could be compared to the stable carbon isotope study above. If burials at CL7 truly represent some individuals who were born in England and some who were born in the colonies, members of each group would be expected to have similar lead isotope values. And if the lead isotope data corroborates the carbon study, the same individuals should cluster together, revealing the vastly different lead environments to which each cluster was exposed. Furthermore, by conducting the same lead isotope tests on local, contemporaneous faunal remains, a good indicator of the local lead environment's early to mid-17th-century isotopic signatures could be obtained. Individuals who spent most of their time in the colonies would align much more closely to this group than those who spent most of their time in England.

As for those individuals who were adolescents at death, their high bone turnover rate may obscure the lead isotope signatures associated with their geographical origins. The problem of using individuals who had not reached maturity by death has not been addressed for lead isotope analyses, but given the high rate of lead remobilization during skeletal remodeling, it is expected that these individuals will have an isotopic signature which aligns with the lead environment they inhabited before death (i.e. perhaps a different lead environment than that in which they were born). Earlier researchers have not dealt with this issue, but because CL7 contains few very children (<15yrs.), it is not expected to pose a significant problem for the present study. As stated above, it is possible that in these cases the results will only identify the lead environment in which the individual spent most of their time, rather than the one in which they were born.

In order to sort out questions of origins based on lead isotopes, a careful research design would need to be implemented. Such a design would establish the diagenetic parameters for CL7 burials, and assess the degree to which post-depositional processes have altered the antemortem lead signatures. A proposal for lead analyses is discussed below.

Due to the poor condition in which most remains were found, diagenetic uptake must be seriously considered. Nearly four centuries of interaction with the burial environment has certainly resulted in diagenetic changes to gross morphology and histological architecture. Fluxes in soil temperature, hydrological processes, soil acidity, microbial activity, recrystallization, and ionic exchanges have all likely contributed in some way to the present state of the College Landing remains. Nevertheless, postmortem uptake must be addressed by any osteoarchaeological study, and the recommendations below will accommodate this.

From the preceding chapters, it should be apparent that any archaeological study of skeletal lead involves two discrete programs: one to account for diagenesis and the other to assay elemental and isotopic composition. The former will be considered first.

SOIL ANALYSIS

Analysis of soil samples has three goals: to determine the pH, lead concentration, and isotopic ratios present. The first factor will help address lead's soil mobility, and can establish a rough parameter for the extent of diagenesis. The second test will characterize the amount of lead present in the soil at the time of excavation, and provide yet another clue as to how severe diagenetic uptake may be. The last analysis will be used to compare isotopic profiles from the burial environment with those found in the bones.

Two different kinds of soil samples should be assayed. One type will represent soils extracted from the graves at the same depth as the remains themselves, and will be referred to as the burial wall soil sample (BWS). A single sample of 300g for each individual to be tested will be sufficient (Carlson 1995:561). The other category of soil sample should be taken from soils directly adhering to the skeletal remains (skeletal remains soil sample, or SRS). The reason for this is to check for lead leaching out of the bones themselves. Finding isotopic signatures characteristic of the skeletal materials in the soil immediately adjacent to the bones would provide yet another parameter for diagenetic characterization. For the best results, approximately 10g of soil clinging to the bones of each individual should be tested for isotopic ratios (Carlson 1995:561). Throughout all of the soil analyses, it is important to run both blank samples (to account for any lead acquired during testing) and standard reference materials (to validate results) exactly

as the soils themselves will be tested. (Standard reference materials are readily available, such as those used in De Muynck *et al.* 2007, 2008.)

Soil collection should be performed very carefully to ensure that no post-excavation lead contaminates any of the samples. In short, samples need to be extracted without using metal instruments containing lead, and should be cleaned between extractions to prevent cross contamination. Either sealed desiccators or air tight receptacles with no known lead content should be used for storage prior to sample preparation and analysis (Carlson 1995:561).

Testing for soil pH is the simplest of the proposed experiments. Twenty grams of soil from the burial walls should be combined with 40ml of deionized water, left to stand for half an hour, stirred well, and left for a full hour. The pH of the soil solution/paste can then be easily tested.

As described in Chapter 3, elemental and isotopic compositions for lead can both be measured from the same sample using ICP-MS. Both the BWS and SRS can be submitted to ICP-MS for quantification following the same protocol (discussed in De Muynck *et al.* 2008:479-480).

Before any analyses can begin, the soil samples need to be “ground to a homogeneous fine powder,” for which a ball mill will suffice (De Muynck 2007:64). Soil samples (0.2g) for elemental and isotopic quantification should then be submitted to microwave-assisted acid digestion, using a combination of HNO₃, HCl, HF, HClO₄ (ratios of 5:2:2:1, respectively). The acids themselves should be purified prior to digestion, via vapor distillation or sub-boiling in quartz equipment (Carlson 1996:561; De Muynck *et al.* 2008:479). Microwave digestion will proceed according to the following program developed by De Muynck *et al.* (2007:64):

20 minutes at 250W
8 minutes at 600W
15 minutes at 250W
20 minutes at 250W
8 minutes at 400W
15 minutes at 250W

After acid digestion, the soil solution should be evaporated at 105°C on a hotplate to complete the dissolution process (De Muynck *et al.* 2007:64). For this step, another acidic solution needs to be added, composed of HNO₃, HF, and HClO₄ at ratios of 1:1:1 (De Muynck *et al.* 2007:64). The resulting residue should then be taken up by HNO₃ (14M under ultrasonic agitation). This new solution needs to be diluted

with ultrapure water (resistivity >18M Ω) to bring the HNO₃ concentration down to 1M (De Muynck *et al.* 2007:63-64).

Once digested, Pb needs to be isolated from the soil matrix. De Muynck *et al.* (2008:479) recommend chromatographic separation “using a column containing a commercially available lead-selective crown ether.” This stage in the sample preparation will separate lead from the rest of the mixture, making it available for quantification (for a discussion of chromatography, see Pollard and Heron 2008:61-66). Chromatographic separation procedures will follow the suggestions of De Muynck *et al.* (2007:65), who recommend the sample solution of 1M HNO₃ be rinsed with 10ml 0.1M HNO₃, followed by elution with 10ml 0.05M (NH₄)₂C₂O₄. This will remove all of the remaining elements in the sample matrix, leaving only the pure lead fraction.

After chromatographic separation, the Pb fraction of the sample is isolated from the other compounds present in the burial soil. However, Pb still needs to be separated from the acid used in the separation procedure [(NH₄)₂C₂O₄]. In order to do this, an aliquot of the sample needs to be evaporated to dryness, after which 1mL 14mol L⁻¹ HNO₃ + 1mL + 10 mol L⁻¹ H₂O₂ should be added. Again, the sample should be evaporated to dryness, whereupon the residue should be “taken up in 0.5 mol L⁻¹ HNO₃ + 0.22 mol L⁻¹ HF” (De Muynck *et al.* 2008:479). The soil Pb, in its final liquid sample state, can then be introduced into the ICP-MS.

A single collector ICP-MS will suffice, since only one element is to be measured. Neon is preferable to argon as the collision gas, principally because it results in a higher analytical precision at a lower rate of flow. Ideally, a flow rate of 0.1ml Ne per minute should be used to optimize precision and reduce the amount of gas used (De Muynck *et al.* 2007:67).

The quantification of Pb isotopes needs to be conducted several times in order to ensure the measurements are as accurate as possible. Fifteen cycles of 46 seconds each (11.5 minutes total) should be measured, although the first four of these can be discounted due to signal fluctuations during the initial runs. The ten remaining cycles will then be used for isotopic quantification, while the first five can be regarded as analytical “stabilization time” (De Muynck *et al.* 2007:67).

SKELETAL ANALYSIS

In order to characterize lead concentrations in the bones from College Landing, appropriate sample selection, preparation, and analytical procedures need to be followed. As with the soil samples, contamination threats need to be assessed and minimized as much as possible to preserve the integrity of the analytical data.

As mentioned earlier, both the human remains from CL7 and faunal samples will be submitted to ICP-MS, the latter to provide a reference for the expected 'background' isotopic ratios for the local 17th-century Tidewater environment. Blank samples and standard reference materials will also need to be run to control for any spurious variables. Recently developed standard reference materials have been created and verified by Hetter *et al.* (2008) and permission has already been obtained for their use.

Where long bones are available, full thickness cores will be taken using an electric drill and hollow, stainless steel bit (Wittmers *et al.* 2008:380). Alternate test sites will be determined upon visual inspection for those individuals for whom long bones are not available, but will consist entirely of cortical tissue. Any adhering trabecular bone will be removed from the samples prior to chemical analysis. It would be ideal to obtain at least two samples from each individual, but this may not be possible given the aforementioned poor state of preservation.

Samples will be mechanically cleaned and submitted to sonification in triple-distilled water for one minute. Afterward, a 0.5mm-thick section from both periosteal and endosteal surfaces will be removed to help limit the amount of diagenetic lead in the final sample. These samples will then be dried at 100°C (Wittmers *et al.* 2008:380), after which they will be pulverized using a bone mill. The resulting powder will then be ready for digestion, isolation, and isotopic quantification.

The bones in this study will be submitted to the same digestion and isolation procedures as those described for the soil samples, with a few minor (but important) differences in the digestion phase. While microwave digestion is preferred for bone, the acids used and microwave program are different. For bone, the acid combinations should be HNO₃ and HCl at a ratio of 4:1. The microwave program will be as follows:

5 minutes at 250W
5 minutes at 400W
5 minutes at 250W

As with the soil samples, the microwave digestion does not completely digest the sample, which must be heated at 105°C on a hotplate to evaporation (De Muynck *et al.* 2007:64). Unlike the soil, however, no additional acids should be used in the hotplate phase.

The isolation (chromatographic column) and ICP-MS procedures are identical for the bone and soil samples. Once all of the data have been measured, comparisons between the isotopic signatures from each sample can be made.

SAMPLE COMPARISONS AND RESULTS

Isotope signatures are best analyzed graphically. Lead composition is traditionally expressed in terms of ratios of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ for archaeological purposes (Carlson 1996:559; De Muynck *et al.* 2008:480). These ratios can be plotted as coordinates ($^{208}\text{Pb}/^{206}\text{Pb}$ as the y-axis, $^{207}\text{Pb}/^{206}\text{Pb}$ as the x-axis) and graphically compared. Samples collected from the burial walls would be expected to align fairly closely with one another, given the close quarters of the College Landing graveyard (i.e. fairly similar biogeochemical processes should be at work).

Samples collected from soil attached to bone (SRS), however, would probably not plot in the same region as the burial wall samples (BWS). It is expected that the degree of diagenetic isotope exchange between soils and bones will vary between burials, but SRS samples would probably fall in the same graphic cluster, distinct from both the BWS and skeletal samples.

Whereas plotting the soil samples gives some indication of diagenetic contributions, data from the faunal and human bones will hopefully discriminate between those who spent most of their time in the colonies and those who spent most of their time in Britain. Based on the stable carbon isotope tests, we might expect CL7-0014 and CL7-0063 to cluster together in a group with isotope signatures distinct from CL7-0065, CL7-0061, CL7-0030, and CL7-0065. If the former truly represent Virginia-born individuals (given their young ages, this may be case), their isotopic signatures should be fairly similar to those observed for the faunal samples. Since few lead artifacts were found at CL7, the contribution of material culture to antemortem lead burdens is likely minimal, although some variations in isotopic signatures between CL7-0014/CL7-0063 and the faunal group may be attributable to anthropogenic lead. The other

group which clustered together in the carbon analysis might have fairly similar isotope signatures, and provide further evidence that there is a clear distinction between where these two groups came from. As for those individuals who were not represented in the stable carbon isotope tests but are appropriate to be sampled for this study, their isotopic signatures would probably group with one of the two clusters mentioned. This may provide a way to infer their origins based on lead isotopes alone.

However, it is entirely possible that the hypothesized clustering effect would not prevail, and an alternate pattern would be in evidence. If this is the case, several different factors may explain the unexpected trends. Firstly, it is possible that the individuals will cluster in two distinct groups whose constituents are not the same as those in the two carbon isotope groups. This may still indicate a sharp difference in origins, but one which is not corroborated by the stable carbon data. If one group still aligns closely with the local contemporaneous faunal group, and the other aligns with a vastly different series of isotope ratios, it is entirely possible that a group of Virginia-born colonists and another exogenous group exist within the CL7 population.

If this is the case, the second hypothesis may be correct. Normal bone metabolism would be expected to alter the lead isotope ratios associated with an individual's original lead environment. If an individual moved to a vastly different geographic region, especially during childhood or early adolescence, then their lead isotope ratios would undergo significant modification (although the extent to which rapid bone remodeling changes an individual's original lead isotope signature is not well characterized, and would be a subject of future research). For CL7, those individuals who most closely align with the faunal remains have probably spent nearly all of their time in colonial Virginia, and would likely cluster tightly together. Anyone at CL7 who arrived after the beginning of adulthood would likely retain much of their Old World lead signatures, and be easily distinguished from those who spent most of their time in Virginia. But those individuals who arrived in Virginia before or during a major bone remodeling phase (again, childhood or early adolescence) would probably not cluster as a single group, but instead show a scattering of lead isotope ratios distinct from the local Tidewater environment. Depending on how similar these individuals' isotopic signatures are to the lead environment around CL7, it may be possible to determine whether or not they spent most of their lives in Virginia or most of their lives abroad. However, without supporting data from other analyses, these conclusions would have to remain tentative.

Secondly, instead of the individuals aligning with one of two groups, the lead analyses may reveal multiple clusters. These would be rather difficult to explain. Because these individuals probably lived within close proximity to one another during the earliest stage of the colony's history, it is improbable that they would have been differentially exposed to distinct material or environmental lead reservoirs. Furthermore, it is unlikely that several different origins would account for a multitude of isotopic ratio clusters in a very small, early 17th-century Tidewater Virginian cemetery. Diagenetic alteration also seems a poor candidate to account for multiple clusters. Unless the individuals within each group are spatially correlated in the graveyard, highly localized biogeochemical processes would not be able to explain the different clusters. In the case of multiple groups, it is advisable to reexamine the analyses to determine whether cross-contamination could have occurred, as this is the most likely explanation for that outcome.

A final alternative worth considering is the total lack of a clustering effect, as predicted by the third hypothesis. Again, given the small size and early historical context of CL7, it is unlikely that differences in origins would account for each individual's unique isotopic ratios. Instead, it is possible that slight variations in how each individual interacted with their material and natural lead environments could explain why no two individual profiles are in alignment. Depending upon when the individual came to Virginia and how soon afterwards they died, their isotopic signatures may not tie them to their original environment, but could instead be in a state of transition due to recent migrations. This would hold especially true for any adolescents, whose rapid bone turnover rate might obscure the isotopic signatures of their original lead environments. What may be more likely, however, is that diagenesis has altered the lead chemistry of each individual to such an extent that any antemortem isotopic similarities have become obscured. If this is indeed the case, the study of CL7 could be more beneficial to our understanding of diagenetic processes than intracemetery population origin variations, and still prove very useful to other studies in bioarchaeological chemistry.

Whatever the possible outcomes, a study of CL7 can have broad implications not only for the bioarchaeology of colonial America, but for archaeological chemistry at large. While the methodologies suggested for this project are not new, their application to this particular research question is. This study has the potential to be the first to discriminate between Old and New World origins for individuals interred around the same time in the same cemetery. Since the people at CL7 likely lived and worked together

closely, they were probably exposed to the same lead environment. However, those who were born and spent most of their time in Britain were exposed to a much different lead environment than those born in Virginia, and isotopic data should reflect this.

Herein lies the excitement of lead analyses. As methodologies improve and research designs become more robust, the kinds of data archaeologists are able to obtain become more refined. This allows investigators to develop means for testing archaeological problems which could not have been addressed even a few years ago. Because skeletal lead speaks to such a diverse array of anthropological interests, its characterization in buried human bone can provide a wealth of information from a single study. With the College Landing population, lead may eventually support a series of chemical tests which can one day determine each individual's origin. Such an analysis cannot alone provide an exact depiction, but it is an important step in holistic archaeological research.

CONCLUSION

Few trace elements found in human bone are as archaeologically descriptive as lead. Given that the toxin is geographically ubiquitous, industrially appealing, and readily absorbed by the mineral phase of the human skeleton, a wide variety of past cultural practices can be studied in the context of metabolized lead. Its residence in bone may speak to the foodways which originally introduced the metal, various occupational exposures, contemporary pathological trends, human mobility through lead environments, commercial activities which made the toxin available, and a variety of other anthropologically relevant phenomena. Archaeologists are seldom given the opportunity to address such a wide variety of human behaviors by looking at a single category of data. In an appropriately drafted research design, assessments of skeletal lead may prove enormously advantageous, and ought to be given due consideration.

From what has been discussed above, it should be obvious that the incorporation of lead analyses into bioarchaeological inquiry is something of a double-edged sword. On the one hand, elemental and isotopic lead has the unique ability to provide data on a host of archaeologically relevant issues ranging from diet and status to cultural affinity and migration. Few other trace elements offer such analytical versatility to modern researchers, and the battery of methodological instrumentation currently available brings nearly any inquiry relevant to bone lead within the purview of archaeological investigation. If carefully executed, skeletal lead assessments can furnish lines of evidence which might otherwise remain unavailable.

On the other hand, lead analyses are not always carefully executed, and can lead to misguided conclusions. Oftentimes, results obtained for skeletal lead burdens from an archaeological population are compromised by the possibility that diagenesis has altered the lead levels from their antemortem quantities. As discussed in Chapter 4, many early researchers were unaware of the complexities of diagenesis and the numerous steps one must follow to control for its parameters. Therefore many of the conclusions these investigators drew would need to be critically reevaluated in order to measure up to the rigorous standards required by modern day research designs.

But whether the data are reliable or not, many archaeologists have hinged entire theories about past social behaviors and processes on skeletal lead assays, with only limited support derived from other evaluations. Clearly, the strongest claims are those which draw upon other information to corroborate

chemical testing. If data derived from lead analyses comprise the only information used to support an archaeological theory, the conclusion must be considered provisional.

The case study presented in the final chapter shows how one can provide some measure of assurance against diagenetic influence, or at least quantify its presence and the degree to which it may have altered the data. This requires a fairly robust soil chemistry program, but if the conclusions are to be sound, post-depositional modifications must be characterized as well as possible. Furthermore, methodological limitations have largely been overcome by incorporating the most appropriate instrumentation for the study at hand. High analytical precision and sensitivity are combined with rigorous quality controls to produce reliable, reproducible data. Equally as important, the conclusions which might be made through such an analysis are intended to be taken into consideration along with the stable carbon isotope tests and material assemblage associated with CL7.

If it can be shown that diagenesis has not significantly influenced the lead isotope ratios found in the CL7 skeletal remains, then the isotopic signatures should reflect the lead environments to which each individual was exposed during life. It is likely that some individuals at CL7 were born in the Virginia Colony, while others probably spent most of their time in Britain before arriving in the New World. Lead isotope signatures should reflect these differences, as those born in Virginia would have been exposed to a much different lead environment than those coming from Britain. Stable carbon isotope analyses have shown that the CL7 population can be divided into two distinct clusters which reflect differential exposure to dietary plant environments. It is hypothesized that the lead isotope assays will produce very similar, if not the same clusters as the carbon isotope tests. Even if the same clusters are not produced, a group of individuals aligning with the local faunal group should be differentiated from those whose original lead isotope signatures have been modified by a change in environment. In this case, it should still be possible to determine who at CL7 spent most of their lives in Virginia, and who spent most of their lives abroad. If either of these results prevails, then a stronger case can be made for the use of lead isotope data for distinguishing between Old and New World population origins/migrations.

It is hoped that the inclusion of a case study is instructive, as it was conceived to demonstrate how to avoid many of the problematic issues associated with lead analysis. But it is also hoped that such a case study demonstrates the surprising utility of this kind of chemical analysis, not only in the type of data one

can gather, but in the interpretations to which that data can be put. As long as one exercises caution and tempers any lead-based conclusions with other lines of evidence, lead-in-bone assessments can become an essential component of any analysis of archaeological human remains. And considering the great strides which have been made in the field during the past five decades, the future may prove lead to be archaeologically useful in ways as yet unimagined.

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